Ste 830-H-15 NAS 1.60:1856

AUG 4 1981

NASA Technical Paper 1856

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JULY 1981

NASA

NASA Technical Paper 1856

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National Aeronautics
and Space Administration

**Scientific and Technical
Information Branch**

1981

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SUMMARY

An analytical study of hydrogen-air kinetics has been performed as part of the scramjet engine research efforts at Langley Research Center. Calculations were made over a range of pressure from 0.2 to 4.0 atm, temperatures from 850 to 2000 K, and mixture equivalence ratios from 0.2 to 2.0. The finite-rate chemistry model included 60 reactions in 20 species of the H_2-O_2-N_2 system. The calculations also included an assessment of the effect of small amounts of the chemicals H_2O, NO_x, H_2O_2, and O_3 in the initial mixture on ignition and reaction times as well as an assessment of the effect of the variation of the third-body efficiency of H_2O relative to N_2 in certain key reactions on reaction time.

The results indicate that for mixture equivalence ratios between 0.5 and 1.7, ignition times are nearly constant; however, the presence of H_2O and NO can have significant effects on ignition times, depending on the mixture temperature. Reaction time is dominantly influenced by pressure but is nearly independent of initial temperature, equivalence ratio, and the addition of chemicals. Effects of kinetics on reaction at supersonic combustor conditions are discussed, and recommendations are made for further experimental studies of rate constants for key reactions.

INTRODUCTION

The study of the fluid dynamics and combustion processes of hydrogen-fueled supersonic combustion ramjets (scramjets) has been a major part of the hypersonic propulsion research program at Langley Research Center. Most of these studies have been, of necessity, experimental investigations of the overall effects of fuel injection, mixing, and reaction on the flow in subscale engine components. This dependence on empirical results is due to the complexity of the flow around fuel injectors in three-dimensional geometries, which are not readily treated analytically. Most numerical solutions are restricted to two- or three-dimensional parabolic flow with equilibrium or simple finite-rate chemistry models of the H_2-air system. Such numerical solution schemes are applicable only in the parabolic flow region well downstream of the disturbance caused by the transverse fuel injection. Scramjet combustors rely on transverse injection of the fuel in order to achieve rapid mixing and reaction. To begin the calculation therefore requires a prior knowledge of the extent of fuel mixing, ignition, and reaction.

All this information, particularly the ignition-reaction state, may not even be available from experimental data because of the difficulty of freezing the reaction in a sample extracted by a probe from the high-velocity, high-temperature combustor flow. In spite of these problems, however, a sufficient data base has been established to define a scramjet engine concept and to permit fabrication of subscale engine models with integrated inlet, combustor, and nozzle components. The current scramjet is designed for operation over a

flight Mach number range from 4 to 7. The corresponding stagnation temperatures of the captured air are 900 K and 2200 K, respectively, which should be sufficient for autoignition of hydrogen in the separated flow regions near fuel injectors. In recent ground tests of subscale engine models (ref. 1), however, problems were encountered in obtaining ignition and sustaining reaction at test conditions for which ignition and reaction might have been expected. The need to better understand the chemical mechanism of the ignition and reaction of H_2-air mixtures at conditions typical of a scramjet combustor led to this study.

The present analytical study uses a computer program (refs. 2 and 3) for solving chemical kinetics problems in one-dimensional flow, with an H_2-O_2-N_2 finite-rate chemistry model consisting of 60 reactions involving 20 species. The calculations covered a range of pressures from 0.2 to 4 atm, a range of temperatures from 850 K to 2000 K, and H_2-air mixtures between 0.2 and 2.0 times the stoichiometric value. In addition, the effects of contaminants such as NO_x and H_2O, which may be present in the high-temperature test gases used in ground test facilities, were investigated. Significant concentrations of NO_x molecules are produced in facilities which use an electric arc to heat the test air; H_2O is produced in combustion-heated facilities as a result of burning hydrogen in air enriched with oxygen so that the airlike products have the proper oxygen mole fraction. (In the latter facilities, the test gas product is sometimes referred to as "vitiated" air.) The effects on ignition times of potential ignition aids such as H_2O_2 and O_3, which may be added to ground test facilities, were also considered. In addition, O_3 is naturally encountered in high-altitude (>30 km) flight. Because the computer program is one-dimensional, the effects of fuel injection and mixing cannot be included. However, the present finite-rate calculations of premixed H_2-air flows are considered important in predicting ignition and reaction in the recirculating zones near the fuel injectors. In analysis of scramjet combustors, where the reaction may be limited by the mixing, these results for premixed reactants provide a lower limit of the times required for reaction.

Many other analytical studies of the chemical kinetics of the H_2-air system, including vitiated air, have been conducted (e.g., refs. 4 to 19). However, many of the problems encountered in scramjet testing have not been addressed explicitly. These include ignition and reaction at low temperatures; varying amounts of water in the vitiated-air test gas; and realistic equilibrium concentrations of oxygen and hydrogen atoms, hydroxyl free radicals, and oxides of nitrogen in the test stream. For example, in the vitiated test gas of a ground test facility at conditions representative of Mach 4 and Mach 7 flight, water mass fractions are about 0.05 and 0.23, respectively. In an arc-heated facility, NO_x mass fractions may range between 0.01 and 0.03. In some of these previous calculations, the chemistry models were too simple to be applied at low-temperature or high-pressure conditions. In some references, the reaction-rate constants were either estimated, because of a lack of data, or they were approximated from early data that precede the survey by Baulch et al. in references 20 and 21. This survey (refs. 20 and 21) along with more recent data (ref. 15) was used to update the rate constants of the H_2-air mechanism.

The purpose of the present one-dimensional calculations is to define the conditions at which chemical kinetics are important in future ground tests of subscale scramjet-engine models and in analyses of the combustor flow using more sophisticated computer codes. The present calculations include (1) the effects of initial temperature, initial pressure, and the equivalence ratio (degree of stoichiometry) of the H_2-air mixture on the ignition and reaction; (2) the effects of contaminants such as H_2O, OH, H, and O present in an equilibrium vitiated test gas; (3) the effects of NO_x on ignition at low temperature; (4) the effects of H_2O_2 and O_3 used to promote ignition in ground test facilities and the effect of atmospheric O_3 that may be encountered in scramjet flight; and (5) the sensitivity of ignition and reaction to the reaction rates of dominant reactions.

SYMBOLS

A	area, m^2
A_j	preexponential constant in rate-constant equation (eq. (19)), $cm^3\text{-}mol^{-1}\text{-}s^{-1}$ or $cm^6\text{-}mol^{-2}\text{-}s^{-1}$
a	species production function (eq. (11))
B_j	activation energy in rate-constant equation (eq. (19))
b	enthalpy production function (eq. (12))
$(C_p)_i$	molar heat capacity of species i, $J\text{-}mol^{-1}\text{-}K^{-1}$
c_p	specific heat at constant pressure, $J\text{-}g^{-1}\text{-}K^{-1}$
f, f^*	local and stoichiometric hydrogen-to-oxygen mass ratios
H_i	molar enthalpy of species i, $J\text{-}mol^{-1}$
h	total-mixture static enthalpy per unit mass, $J\text{-}g^{-1}$
h_c	total-mixture energy per unit mass, $J\text{-}g^{-1}$
K_j	equilibrium constant
k_{bj}	backward reaction-rate constant
k_j	forward reaction-rate constant
ℓ	number of chemical reactions
M	Mach number; third-body species in certain reactions
M_j	third-body efficiency factor defined by equation (25)
$(MW)_i$	molecular weight of species i, $g\text{-}mol^{-1}$

$\dot{m}$	mass flow rate, g-s^{-1}
$m_{i,j}$	third-body efficiency factor of species i in reaction j (see eq. (26))
N	number of species in gas mixture
n_j	temperature exponent in rate-constant equation (eq. (19))
p	pressure, atm (1 atm = 101.325 kPa)
R	universal gas constant, 1.987 cal-mol^{-1}-K^{-1} (1 cal = 4.184 J)
s_i	species i (eq. (18))
T	temperature, K
t	time, s
u	velocity, m-s^{-1}
W_i	net species production rate (eq. (21))
W_m	mixture molecular weight, g-mol^{-1}
α_i	mass fraction of species i
Γ	ratio of reaction times
γ	specific-heat ratio
λ	ratio of ignition times
ν_{ij}	forward stoichiometric coefficient in general reaction (eq. (18))
ν'_{ij}	reverse stoichiometric coefficient in general reaction (eq. (18))
ρ	density, kg-m^{-3}
σ_i	concentration of species i, moles per unit mass of mixture, mol-g^{-1}
τ_{ig}	ignition time, s
τ_R	reaction time, s
τ_{TR}	total reaction time, s

ϕ	equivalence ratio, f/f*
ψ_j	net conversion rate in kinetics equations
ω_{ij}	net rate of formation of ith species in reaction j

Subscripts:

eq	equilibrium
i	species (i = 1, 2, . . ., N)
j	reaction (j = 1, 2, . . ., ℓ)
o	initial conditions
r	reference conditions

Abbreviations:

EFS	equilibrium free stream
ppmw	parts per million by weight

ANALYSIS

Differential Conservation Equations

The computer program used for this analysis of a complex reacting gas mixture flowing through an arbitrarily assigned area employs the conservation equations for one-dimensional steady-state flow. The flow is assumed to be isobaric, premixed, inviscid, and adiabatic. Additional information about these equations and the numerical integration procedure used in the computer code may be found in references 2 and 3. The equations employed are

Global mass conservation

$$\rho A u = \dot{m} \tag{1}$$

Continuity for each of the N species in the mixture

$$\frac{d}{dt}(\sigma_i \dot{m}) = W_i A u \qquad (i = 1, 2, \ldots, N) \tag{2}$$

where σ_i is the concentration of species i, in moles per unit mass of the mixture, and W_i is the species production rate. Expanding the differentiation of equation (2), using equation (1), and noting that $d\dot{m}/dt = 0$ reduces the equation to

$$\frac{d\sigma_i}{dt} = \frac{W_i}{\rho} \qquad (i = 1, 2, \ldots, N) \qquad (3)$$

Conservation of momentum

$$\rho \frac{du}{dt} + \frac{1}{u} \frac{dp}{dt} = 0 \qquad (4)$$

Conservation of energy

$$h + \frac{u^2}{2} = h_c \qquad (5)$$

where h_c is the total constant energy per unit mass of the gas and the mixture molecular weight is defined as

$$W_m = \left[\sum_{i=1}^{N} \sigma_i \right]^{-1} \qquad (6)$$

Equation of state

$$p = \frac{\rho RT}{W_m} \qquad (7)$$

By use of equations (1) to (7), the following differential equations can be derived, with time t the independent variable:

$$\frac{du}{dt} = \frac{u}{M^2 - 1} \left(\frac{1}{A} \frac{dA}{dt} - a \right) \qquad (8)$$

$$\frac{d\rho}{dt} = -\rho \left[\frac{M^2}{M^2 - 1} \left(\frac{1}{A} \frac{dA}{dt} - a \right) + a \right] \qquad (9)$$

$$\frac{dT}{dt} = -T\left[\frac{(\gamma - 1)M^2}{M^2 - 1}\left(\frac{1}{A}\frac{dA}{dt} - a\right) + b\right] \tag{10}$$

where

$$a = \frac{RT}{p}\sum_{i=1}^{N} W_i - b \tag{11}$$

and

$$b = \frac{1}{p}\frac{\gamma - 1}{\gamma}\sum_{i=1}^{N} h_i W_i \tag{12}$$

Other parameters used in these equations are defined as follows:

$$M^2 = \frac{u^2 W_m}{\gamma RT} \tag{13}$$

$$\gamma = \frac{c_p}{c_p - (R/W_m)} \tag{14}$$

$$c_p = \sum_{i=1}^{N} \sigma_i (C_p)_i \tag{15}$$

$$h = \sum_{i=1}^{N} \sigma_i H_i \tag{16}$$

$$H_i = (H_i)_{T_r} + \int_{T_r}^{T} (C_p)_i \, dT \tag{17}$$

Equations (3) and (8) to (10) form a system of $N + 3$ equations in $N + 3$ unknowns. This equation system is solved by numerically integrating with time for a specified area distribution. The equation set for a specified pressure distribution and for the passage of a normal shock through the gas is given in reference 2.

Chemical Reaction Equations

Each chemical reaction can be written in the general form

$$\sum_{i=1}^{N} \nu_{ij} s_i \underset{k_{bj}}{\overset{k_j}{\rightleftharpoons}} \sum_{i=1}^{N} \nu'_{ij} s_i \tag{18}$$

where s_i represents the ith species. The forward reaction rate is given by

$$k_j = A_j T^{n_j} \exp(-B_j/RT) \tag{19}$$

The backward reaction rate is determined from k_j and the equilibrium constant K_j:

$$k_{bj} = \frac{k_j}{K_j} \tag{20}$$

The rate of formation of each species W_i which appears in equation (3) is defined as

$$W_i = \sum_{j=1}^{\ell} \omega_{ij} \tag{21}$$

where

$$\omega_{ij} = \rho^2(\nu'_{ij} - \nu_{ij})\psi_j \tag{22}$$

is the net rate of formation of species i by reaction j. The parameter ψ_j is the net reaction conversion rate introduced in reference 2 as an indication of the amount of change due to each reaction that occurs in the mixture. The form of ψ_j depends on the type of reaction. Three types of reversible chemical reactions are considered in the computer program:

Type 1 - Bimolecular shuffle reaction

$$s_1 + s_2 \underset{\leftarrow}{\overset{k_j}{\rightarrow}} s_3 + s_4$$

with

$$\psi_j = k_j\left(\sigma_1\sigma_2 - \frac{\sigma_3\sigma_4}{K_j}\right) \tag{23}$$

Type 2 - Three-body recombination

$$M + s_1 + s_2 \underset{\leftarrow}{\overset{k_j}{\rightarrow}} s_3 + M$$

(where M can be any species present) with

$$\psi_j = k_j M_j\left(\rho\sigma_1\sigma_2 - \frac{\sigma_3}{K_j}\right) \tag{24}$$

In this equation, M_j is the third-body efficiency factor for the jth reaction defined as

$$M_j = \sum_{i=1}^{N} m_{i,j}\sigma_i \tag{25}$$

and $m_{i,j}$ is the third-body efficiency factor for species i in reaction j. This factor is a correction to the preexponential factor A_j in the rate equation (19) and can be written as

$$m_{i,j} = \frac{(A_j)_{s_i}}{(A_j)_r} \tag{26}$$

where $(A_j)_r$ is the value of A_j for a reference species as third body. For the calculations presented in this paper, all third-body efficiencies are referenced to N_2. Except as listed at the bottom of table I, all third-body efficiencies are 1.0.

Type 3 - Two-body dissociation

$$M + s_3 \underset{\leftarrow}{\overset{k_j}{\rightarrow}} s_1 + s_2 + M$$

with

$$\psi_j = k_j M_j \left(\sigma_3 - \frac{\rho\sigma_1\sigma_2}{K_j} \right) \tag{27}$$

For some problems the heat release is an important consideration. In these situations a useful quantity is the net energy conversion rate for the jth reaction defined as

$$(\psi_H)_j = \psi_j (\Delta H_{298})_j \tag{28}$$

where $(\Delta H_{298})_j$ is the molar heat of reaction at 298 K for the jth reaction proceeding in the forward direction, from left to right.

Computer Program

The computer program for solving the one-dimensional flow with finite-rate chemical reactions was first presented in reference 2. The system of conservation equations and chemical reactions form a nonlinear, coupled set of differential equations, which are solved by the Adams implicit method (ref. 22). A later modification of the computer code (ref. 3) added the stiffly stable, linear, multistep method of Gear (ref. 23). The incorporation of the Gear method into the program provides a solution technique that is a highly efficient means of altering step size to obtain a stable rapid solution to the large system of stiff equations. This is of particular advantage when the number of chemical species is greater than 15.

Input to the computer program is user oriented. This allows for easy modification to the chemical reaction system, reaction-rate parameters, thermodynamic properties (ref. 24) and general problem specification. Additional details of the input specifications are given in reference 3.

Scope of Present Calculations

The objective of the present study is to parametrically examine the ignition and reaction times of H_2-air mixtures at conditions representative of scramjet combustor flows. The ignition time, also known as ignition delay or induction time τ_{ig}, is the time required for the rapid buildup of the free radicals and atoms with very little heat release. Three definitions of ignition time have been used in previous research: (1) the time for the concentration of OH to reach 5×10^{-9} mol/cm^3, (2) the time at the end of the constant exponential growth of OH mass fraction, and (3) the time taken to reach a temperature at ignition T_{ig} of

$$T_{ig} = 0.05(T_{eq} - T_o) + T_o \tag{29}$$

The ignition time given by definition (1) was used only for comparison with the experimental data of reference 15. It was observed that the ignition times given by definitions (2) and (3) are approximately the same over a wide range of pressure and temperature. The ignition-time results from these calculations are therefore presented using equation (29). The total reaction time τ_{TR} is defined as the time taken to reach a temperature T_{TR} where

$$T_{TR} = 0.95(T_{eq} - T_o) + T_o \tag{30}$$

Reaction time is then defined as

$$\tau_R = \tau_{TR} - \tau_{ig} \tag{31}$$

Chemistry model.- The chemical reaction model, given in table I, consists of 60 (ℓ = 60) reactions involving 20 (N = 20) species:

O_2	N_2	H_2	O	N	H
H_2O	OH	HO_2	NO	NO_2	
CO	CO_2	HNO	HNO_2	HNO_3	
H_2O_2	O_3	HCO	Ar		

Reaction-rate data were taken from references 14, 20, 21, and 25 to 32. These data are some of the latest available for the hydrogen oxidation mechanism and provide improvements to the reaction-rate parameters and third-body efficiency factors for certain key reactions such as

$$H + O_2 + M \rightarrow HO_2 + M$$

$$NO + HO_2 \rightarrow OH + NO_2$$

and

$$H + OH + M(H_2O) \rightarrow H_2O + M(H_2O)$$

The impact of the reaction rates and third-body efficiencies of these reactions on ignition and reaction is discussed in the section "Reaction Time."

Parameter variation.- The principal parameters of these calculations are the initial static pressure and temperature and the hydrogen-air mixture composition. Static pressures were varied between 0.2 and 4.0 atm; static temperatures between 850 and 2000 K. The amount of hydrogen in the initial mixture was varied corresponding to equivalence ratios between 0.2 and 2.0. The equivalence ratio ϕ is an indication of the relative stoichiometry of the mixture based on the global reaction for the oxidation of hydrogen:

$$2H_2 + O_2 \rightarrow 2H_2O$$

For this reaction the stoichiometric mass ratio of hydrogen to oxygen is

$$f^* = \frac{(\text{moles } H_2)(MW)_{H_2}}{(\text{moles } O_2)(MW)_{O_2}} = \frac{2(2.016)}{1(32)} = 0.126 \qquad (32)$$

For an arbitrary mixture of hydrogen and air (or other species) with a mass ratio of hydrogen to oxygen f, the equivalence ratio is defined as

$$\phi = \frac{f}{f^*} \tag{33}$$

Most of the calculations were made for $\phi = 1.0$.

Chemical additives and contaminants.- In addition to the variation in the state properties, the composition of the air was varied to study the effects of contaminants (H_2O, NO_x) present in ground test facilities and chemical additives (H_2O_2, O_3) used as potential ignition aids in ground tests of subscale scramjet engines. In order to simulate the combustor conditions of a scramjet at Mach 4 to Mach 7 flight, it is necessary to heat the air in ground test facilities. One way to produce a high-temperature test gas is to burn hydrogen in oxygen-enriched air. The test gas produced by such a combustion heater facility (ref. 33) is often referred to as vitiated air, since it has the same oxygen mole fraction as air but is contaminated by a significant concentration of water vapor. The amount of H_2O present in the vitiated test gas is directly related to the desired stagnation temperature (or flight Mach number) that is simulated. For this analyis, the following values of water mass fractions are assumed to form a consistent set with each of the initial temperatures:

T_o,K	910	1000	1100	1200	>1300
α_{H_2O}	0.097	0.125	0.145	0.20	0.245

Whereas previous analyses have accounted for vitiation effects by arbitrarily varying the concentraton of H_2O and OH free radicals at the same initial temperature, the consistent pairs of water mass fractions and initial temperatures used in the calculations here provide a more realistic means of assessing the effects of vitiated air on ignition and reaction.

Another scramjet ground test facility (ref. 1) uses an electric arc to heat the air and produces significant amounts of nitrogen oxides NO and NO_2. It has been estimated that this facility produces total NO_x mass fractions of about 0.01 and 0.03 at conditions simulating Mach 4 and Mach 7 flight, respectively. Calculations were made to ascertain the effects of NO and NO_2 mass fractions of 0.01 on the ignition times of the H_2-air mixtures.

In addition, the effects of free radicals that may be present in the test gas as a result of dissociation at the high temperatures were examined. The amount of each free radical present was determined by assuming that the air or vitiated air of the mainstream test gas was in chemical equilibrium at the initial pressure and temperature. Thus, for calculations of H_2 in equilibrium air, small amounts of O, NO, and NO_2 were included in the initial mixture. For H_2 in equilibrium vitiated air, small amounts of O, H, OH, HO_2, NO, and NO_2 were included in the initial mixture. In the following discussion, the results obtained with equilibrium free-stream (EFS) mixtures are referred to

as H_2-air (EFS) and H_2-vitiated air (EFS) to denote hydrogen mixed with equilibrium air and equilibrium vitiated air, respectively. In the vitiated-air facility, the test gas would likely be in equilibrium at the local temperature and pressure at the combustor entrance. However, the arc-heater facility would produce high levels of NO_x (mass fractions of 0.01 to 0.03) that would freeze as the flow expanded through the facility nozzle, so that a true equilibrium would not be obtained.

The effect of small amounts (mass fractions of 0.01) of H_2O_2 and O_3 on ignition was examined to assess their potential as ignition aids in ground tests. Calculations were also made with an O_3 concentration of 10 ppmw to approximate the atmospheric levels encountered in flight at an altitude of 30 km. Maximum O_3 concentration in the atmosphere is about 13.5 ppmw at 36 km (ref. 34).

RESULTS AND DISCUSSION

The one-dimensional kinetics computer code (refs. 2 and 3) previously described was used to calculate ignition and reaction times for the range of parameters indicated. Typical output of the computer code is presented in figure 1 in the form of the time variation of species mass fractions through the ignition and reaction zones. Results are given for a stoichiometric H_2-air mixture at an initial temperature of 1000 K and at initial pressures of 0.5 and 2.0 atm in figures 1(a) and 1(b), respectively, and for a stoichiometric mixture of H_2 in equilibrium vitiated air at T_o = 1000 K and p_o = 1 atm in figure 1(c). The times of ignition and total reaction are noted on each figure by τ_{ig} and τ_{TR}, respectively. The effect of increased pressure to shorten reaction time can be seen by the much smaller difference between τ_{TR} and τ_{ig} in figure 1(b), at 2.0 atm, when compared with the difference indicated in figure 1(a), at 0.5 atm.

Ignition Times

The effects of initial pressure and temperature on ignition time of a stoichiometric H_2-air mixture are presented in figures 2(a) and 2(b), respectively. Because of the widespread use of ignition times from reference 4, τ_{ig} results as given by reference 4 are plotted for comparison as dashed lines in figure 2(a). In contrast to the constant slope with pressure of the reference 4 ignition times, the present results indicate a drastic nonlinearity in the pressure dependence, particularly at values of T_o below 1100 K. At T_o above about 1200 K, the present results indicate a slight retardation of ignition times relative to those given in reference 4. The constant-pressure curves of τ_{ig} as a function of the reciprocal temperature in figure 2(b) indicate very long ignition times as T_o decreases. These effects produced by the present chemical mechanism are primarily due to the formation of the HO_2 molecule through the reaction $H + O_2 + N_2 \rightarrow HO_2 + N_2$, which was not included in the kinetics model of reference 4. This reaction is a chain

terminating reaction which depletes H atoms. Because it is a three-body reaction, it should become more important at higher pressures. Since the reaction rate is weakly dependent on temperature, this reaction is important at low temperatures, where the chain carrier reactions are slower.

The sensitivity of ignition times to the fuel equivalence ratio was checked for H_2-air and H_2-vitiated air at 1200 K and 1.0 atm. Results of these calculations are given in figure 3 along with previous results for H_2-air from references 8, 16, and 19. Also included in figure 3 are data for 1111 K and 1389 K taken from reference 18 in the format presented in reference 17. The present ignition times agree reasonably well with the referenced results, a spread of about 20 percent in τ_{ig} occurring for ϕ between 0.5 and 1.7. In comparison with the data, the present predictions of ignition time at 1200 K show the same trend with increasing ϕ and fall between the data for 1111 K and 1389 K. For both H_2-air and H_2-vitiated air, ignition times predicted by the present chemistry model exhibit only a ±10 percent variation for ϕ in the range from 0.5 to 1.7, although the ignition times for H_2-vitiated air are longer than for H_2-air by about 20 percent. This result supports the conclusion of reference 4 that τ_{ig} is constant for ϕ between 0.4 and 2.0.

In order to test the correctness of the ignition times predicted by the present chemistry model, the theoretical results have been compared with stoichiometric H_2-air shock-tube data from reference 15. These comparisons are presented in figure 4(a) for initial pressures of 0.5 and 2.0 atm and in figure 4(b) for initial pressures of 0.27 and 1.0 atm. The agreement between theory and data is quite good, except for $p = 0.27$ atm in figure 4(b). The authors of reference 15 reported that these low-pressure data were the least reliable because of boundary-layer growth in the shock tube.

A cross plot of these reference 15 data at $T_o = 1000$ K is given in figure 5 with theoretical predictions from references 4 and 14 and the present calculations for comparison. The present results agree well with the data except at the low-pressure ($p = 0.27$ atm) datum. The theory of reference 14 includes a sophisticated chemistry model with 25 reactions. It includes hydroperoxyl (HO_2) and hydrogen peroxide (H_2O_2) molecules and shows the proper trend, although it does not agree with the data. Since the chemistry model of reference 4 did not include the HO_2 reactions, it would not be expected to agree with the data at high pressures (>1.0 atm), where the HO_2 molecule becomes important. The linear relation between τ_{ig} and p of reference 4 does, however, agree with the data in the narrow range of pressures between 0.5 and 1.0 atm at $T_o = 1000$ K.

Effect of vitiated air.- Some scramjet ground test facilities (ref. 33) rely on the combustion of H_2 to produce the desired high-temperature test gas. Because the resulting vitiated-air test gas is contaminated with high concentrations of H_2O, the effect of this contaminant and its dissociation products on ignition times has been examined. A comparison of ignition times for stoichiometric H_2-air (EFS) and H_2-vitiated air (EFS) is presented in figure 6. In figure 6(a), in which the effect of T_o on the variation of τ_{ig} with p is presented, it can be seen that at T_o less than 1100 K and p_{ig} greater than 0.2 atm, the presence of H_2O in the vitiated test gas retards

ignition, particularly at the lower value of T_o. At temperatures above 1200 K, the effect of the vitiation is to enhance ignition. The reason for the longer ignition time at $T_o < 1100$ K is that in a vitiated-air stream, the production of HO_2 is accelerated by the reaction $H + O_2 + H_2O \rightarrow HO_2 + H_2O$ because the third-body efficiency of H_2O may be as much as 13 times that of N_2. Although some OH radicals are present in the free stream, the foregoing reaction tends to deplete H atoms, an important chain carrier in the ignition region, and cause an increase in ignition times.

At temperatures above 1200 K, ignition is enhanced by the dissociation of H_2O in the vitiated free stream and the resulting production of OH radicals, whose concentration (10^{-5} to 10^{-3} by mass) is significantly greater than the mass concentration of O and H atoms. The curves of τ_{ig} versus reciprocal temperature ($1000/T_o$) at constant p in figure 6(b) also illustrate the effect of a vitiated free stream on ignition times. Other calculations (refs. 7 and 16) exhibit similar effects at low T_o over a limited pressure range. Therefore, at low initial temperatures, the ignition characteristics observed in ground tests of scramjet combustors using a vitiated stream are longer than those for tests with air at similar conditions. At the higher initial temperatures, the ignition times are shorter with a vitiated stream.

Effect of equilibrium free stream.- Figure 6 compares the difference between air and vitiated-air free streams when both are in chemical equilibrium. The effect on τ_{ig} of the free radicals produced by the dissociation of H_2O in the vitiated air at chemical equilibrium can be seen from the curves in figure 7. This comparison is made for $\phi = 1.0$ at $T_o = 1300$ K. For H_2-air (solid lines), the presence of O and NO in an EFS ($\alpha_O = 1.3 \times 10^{-8}$, $\alpha_{NO} = 4 \times 10^{-4}$) has little effect on the ignition times. For the H_2-vitiated air (dashed lines), in which $\alpha_{H_2O} = 0.245$, the assumption of EFS at $T_o = 1300$ K produces OH, O, H, and NO ($\alpha_{OH} = 1.5 \times 10^{-5}$, $\alpha_O = 6 \times 10^{-8}$, $\alpha_H = 1 \times 10^{-11}$, $\alpha_{NO} = 3.5 \times 10^{-4}$), which reduce ignition times by about 40 percent. Note that for the vitiated air in which the H_2O is not dissociated (not in equilibrium), the values of τ_{ig} for these conditions are larger than for air. These comparisons suggest that care must be exercised when applying theoretical results to insure that the effects of vitiation are properly accounted for. The investigation reported in reference 35 emphasized the necessity of considering free radicals when comparing theory with combustion data for parallel H_2 injection into a vitiated test stream. Reference 8 also indicated a sensitivity of τ_{ig} to the amounts of H, O, and OH.

Effect of H_2O.- The presence of H_2O in vitiated air has been shown to strongly affect calculated ignition times, particularly at initial temperatures of 1000 K or less. The magnitude of the effect depends on (1) the amount of H_2O present in the initial mixture and the corresponding amounts of free radicals such as OH present in an equilibrium free stream, and (2) the third-body efficiency of H_2O through its effect on the rate of reaction of $H + O_2 + M \rightarrow HO_2 + M$. Graphical representations of these two influences are presented in figures 8 and 9, respectively. In figure 8, the sensitivity of τ_{ig} to mass fractions of H_2O of 0 (air), 0.145, and 0.245 in an initial mixture at $T_o = 1000$ K, is presented for conditions of EFS (dashed lines) and

with H_2O only (solid lines). At a pressure of 0.2 atm the calculated ignition times for all cases range over ±20 percent; however, as the pressure is increased to 1.0 atm, the presence of H_2O alone tends to increase τ_{ig} by a factor of up to 10 for $\alpha_{H_2O} = 0.145$ and up to 30 for $\alpha_{H_2O} = 0.245$. This increase in τ_{ig} is due to the depletion of H atoms by the previously mentioned hydroperoxyl (HO_2) chain terminating reaction. When equilibrium free stream is used, the ignition times are reduced as pressure increases to 1.0 atm by a factor of about 3, relative to the case with H_2O only. This reduction is due to the increased levels of OH.

The sensitivity of ignition times to the third-body efficiency of H_2O, i.e., $m_{H_2O,4}$ in the reaction $H + O_2 + M \rightarrow HO_2 + M$ at $T_o = 1000$ K is presented in figure 9. The computer program currently uses a value $m_{H_2O,4} = 13$ relative to the third-body efficiency of N_2. A change in $m_{H_2O,4}$ in the preceding reaction causes a corresponding change in the rate of the reaction with H_2O as the third body. The effect of increasing and decreasing $m_{H_2O,4}$ by a factor of 2 is illustrated in figure 9 for vitiated air (EFS) with $\alpha_{H_2O} = 0.145$ at $T_o = 1000$ K. Also shown is the case for air (EFS) with no H_2O. At pressures near 0.2 atm, the presence of H_2O with its high third-body efficiency has little effect on τ_{ig} values. As the initial pressure approaches 1.0 atm, the calculated ignition times show a large sensitivity to the value of $m_{H_2O,4}$: doubling $m_{H_2O,4}$ increases τ_{ig} by a factor of 10 at 1 atm; halving $m_{H_2O,4}$ reduces τ_{ig} by a factor of 2 and gives values of τ_{ig} near those of H_2-air (EFS). These results emphasize the importance of knowing the efficiency of H_2O relative to N_2 in modeling the chemistry and in predicting ignition times of H_2 in a vitiated air stream at static temperatures of 1000 K or less and pressures near 1.0 atm.

The sensitivity of ignition times to varying concentrations of NO is presented in figure 10 for H_2-air and H_2-vitiated air at $T_o = 910$ K. For H_2-air in figure 10(a) at low pressures (near 0.2 atm), a concentration of NO of as much as 0.01 by mass has little effect on the ignition time, causing a reduction of less than 20 percent in τ_{ig} for pure air. As the initial pressure approaches 1.0 atm, however, an NO mass fraction of 0.01 reduces τ_{ig} by a factor of 50. For an NO mass fraction of 10^{-5} (10 ppmw), which is the NO concentration in air in equilibrium at 910 K, τ_{ig} is reduced by about a factor of 4. The experimental results reported in reference 15 indicated reductions in τ_{ig} by factors of 2/3 and 1/2 at pressures of 0.27 and 0.5 atm, respectively, due to molar concentrations of NO_x between 0.005 and 0.01. For a stoichiometric H_2-air mixture, the mass fraction of NO_x is about 1.5 times the mole fraction. These results, indicated by squares in figure 10(a), agree reasonably well with the present calculations. Data for shock-tube ignition of H_2-air at 910 K (ref. 36), denoted by the circles in figure 10(a), also show good agreement with the preset calculations.

Figure 10(b) shows that for H_2-vitiated air, increasing the mass fraction of NO in the initial mixture from 10^{-5} (the EFS value) to 0.01 causes significant reductions in τ_{ig}, particularly at pressures greater than 0.5 atm. For an NO mass fraction of 0.01, the ignition times for both H_2-air and H_2-vitiated air are nearly equal. The chemical mechanism responsible in part for these reductions is the reaction $NO + HO_2 \ddagger OH + NO_2$, which produces the active chain carrier OH through the depletion of HO_2. Because HO_2 is formed through a chain terminating reaction that depletes H atoms, it is responsible for the retarding of ignition in vitiated-air mixtures. A more complete mechanism for the effect of NO_x on H_2-air ignition is proposed in reference 37. The results in figure 10 indicate at strong influence of NO on ignition times at low temperature and pressures above 0.5 atm.

Effect of other chemical additives.- Because of the difficulty of obtaining ignition in a short time (or distance) at the low temperatures (850 to 1000 K) and pressures (0.30 to 1.0 atm) typical of a scramjet combustor, certain chemicals have been considered to prompt ignition. These chemicals, such as H_2O_2 and O_3, would supply OH free radicals and active oxygen atoms which would shorten the ignition time. The oxides of nitrogen or other nitrogen compounds which produce these molecules could be used over a limited range of pressures and temperatures. The reduction in ignition times for stoichiometric mixtures of H_2-air and H_2-vitiated air at 1.0 atm obtained by adding mass fractions of O_3, H_2O_2, NO, and NO_2 of 0.01 is presented in figures 11(a) to 11(d), respectively. The reduction in τ_{ig} is given by the parameter λ defined as the ratio of τ_{ig} with the chemical additive to τ_{ig} from figure 6. Chemicals O_3 and H_2O_2 provide substantial reduction in ignition times at all temperatures for both air and vitiated air. Although not presented, reduction of the pressure to 0.5 atm was observed to have little effect on the reduction of τ_{ig} for both O_3 and H_2O_2. For the NO_x additives in figures 11(c) and 11(d), the significant reduction occurs only at the lower temperatures (less than 1100 K). This large reduction in τ_{ig} at the low temperatures occurs because of the same chemical mechanism discussed in the previous section - the formation of OH through the depletion of HO_2 reacting with NO.

The effect of atmospheric O_3 encountered in the flight of a scramjet engine also was examined. At altitudes of about 30 km the O_3 concentration is approximately 10 ppmw. Peak O_3 concentration is about 13.5 ppmw at 36 km. The reduction in ignition time for a trace O_3 concentration of 10 ppmw at 1 atm is given in figure 12. Substantial reduction occurs at the lower initial temperatures (less than 1000 K). Lowering the pressure from 1.0 to 0.5 atm did not change the result.

Reaction Time

In the present analysis the reaction time is defined as the time difference between the ignition time and the total reaction time required to achieve 95 percent of the equilibrium temperature rise (see eqs. (30) and (31)). The effect of pressure on the variation of reaction time with temperature is presented in figure 13 for stoichiometric mixtures of H_2-air and H_2-vitiated air. In contrast to the ignition time, vitiated air has a negligible effect

on the reaction time. In the semilog plot of figure 13, the variation of τ_R with T_o is linear and shows a strong dependence on p. The present calculations also indicate that τ_R is independent of (1) the initial concentration of free radicals and atoms (similar results were reported in refs. 7 and 8); (2) the presence of chemical additives such as NO, H_2O_2, and O_3; and (3) within ±10 percent, the mixture equivalence ratio in the range 0.5 to 1.5. These reaction times can be correlated, within ±10 percent, by the equation

$$\tau_R = 325p^{-1.6} \exp(-0.8T_o/1000) \qquad (34)$$

A comparison of the correlation given by equation (34) and reaction times from references 4, 7, and 8 is given in figure 14 for a stoichiometric H_2-air mixture at p = 1.0 atm. The large difference between the present results and the earlier work of reference 4, which gave reaction times as much as 5 times faster than the present theory, can be traced back to the rate constants for three-body recombination exothermic reactions.

Effect of changes in reaction-rate constants.- One reaction which has a major effect on the calculated reaction time is $H + OH + M \rightarrow H_2O + M$. The reaction rate constant k_3 for this reaction in the present chemical model is similar to the value recommended in references 20 and 21 with N_2 as the third body with an efficiency of 1. However, the rate data of references 20 and 21 exhibited considerable scatter, with a factor of 7 representative of the upper limit change in the rate constant. This factor of 7 was used to increase the rate constant (k_3) and reaction times recomputed. No estimate of the lower limit change was attempted. The comparative effect on τ_R of this change in k_3 by a factor of 7 is presented in figure 15 for stoichiometric mixtures of H_2-air and H_2-vitiated air at pressures of 0.5 and 1.0 atm. For each pressure, the upper curves are for the value of k_3 given in table I; the lower curves are for a rate constant of 7 times k_3. In both cases, the third-body efficiency of H_2O was $m_{H_2O,3} = 6$ (see table I). The effect of the factor of 7 and the high efficiency of H_2O mean that the rate constant for the reaction $H + OH + H_2O \rightarrow H_2O + H_2O$ will have a coefficient $A_3 = 2.2 \times 10^{23}$ compared with the table I value of $A_3 = 0.52 \times 10^{22}$ for the reaction $H + OH + N_2 \rightarrow H_2O + N_2$. The result, shown in figure 15, is a reduction in reaction time by a factor of about 3. The calculated values of τ_R with the faster rate constants agree better with previous results and fall between the τ_R values from references 4 and 7 (compare fig. 14 with fig. 15(b)).

Effect of third-body efficiency of H_2O.- Another way to affect reaction time is to change the reaction rate through the third-body efficiency of H_2O in the reaction $H + OH + H_2O \rightarrow H_2O + H_2O$. In reference 38 this reaction is considered the dominant path for the production of H_2O, with a rate constant of approximately 2.7×10^{17} cm^6-mol^{-2}-s^{-1} at 1650 K. In reference 39, the rate constant had to be $2.4 \times 10^{17} \exp(500/RT)$ cm^6-mol^{-2}-s^{-1} to agree with their data. In the present chemical mechanism the rate constant, including a third-body efficiency factor of 6 for H_2O, is 2.6×10^{21} $T^{-1.5}$ cm^6-mol^{-2}-s^{-1}.

This value is approximately the value recommended by references 20 and 21. A comparison of the three rate constants for the production of H_2O is given in the following table:

T_o, K	Source	k_3, cm^6-mol^{-2}-s^{-1}
1500 ↓	Ref. 38	2.7×10^{17}
	Ref. 39	2.8×10^{17}
	Present study	4.5×10^{16}

In order to check the sensitivity of τ_R to a change in this rate of reaction, the third-body efficiency of H_2O was varied from 1 to 40, with the latter value corresponding to the rate constants from references 38 and 39. Note that the value of the rate constant for the present calculations includes the factor of 6 for the third-body efficiency of H_2O. The effect on τ_R of varying $m_{H_2O,3}$ from 1 to 40 is presented in figure 16 for T_o = 1500 K, p = 1 atm, and stoichiometric mixtures of H_2-air and H_2-vitiated air. These results are represented by the parameter Γ, defined as the ratio of τ_R to τ_R for H_2-air from figure 13, with $m_{H_2O,3} = 6$. The spread between the H_2-air and H_2-vitiated air reaction times disappears when the third-body efficiencies of H_2O and N_2 are equal $\left(m_{H_2O,3} = 1\right)$ and increases to a difference of a factor of 2 when $m_{H_2O,3} = 40$, giving a rate constant of 3.0×10^{17} cm^6-mol^{-2}-s^{-1}.

It is apparent from the comparisons of figures 15 and 16 that the rate constants for the recombination of H and OH to form H_2O will have an important impact on reaction times in scramjet combustors. These results point out the need for more accurate rate data for this reaction with N_2 and H_2O as third bodies.

CONCLUDING REMARKS

An analytical study of the chemical mechanism involved in the ignition and reaction of the H_2-air system has been performed at conditions representative of a scramjet combustor. The calculations were made with a one-dimensional kinetics program with an H_2-O_2-N_2 finite-rate chemistry model consisting of 60 reactions in 20 species. An objective of these calculations was to provide information for an assessment of the conditions at which kinetics are important in scramjet combustors. Specifically, the study considered how ignition and reaction times are affected by initial temperature and pressure; fuel equivalence ratio; the presence of contaminants such as H_2O, H, OH, and NO_x; chemical additives H_2O_2 and O_3; and the reaction rate of key reactions.

Results of the calculations indicated that, within a 20 percent error, ignition time is nearly constant over a range of equivalence ratios from 0.5 to 1.7. Relative to air in chemical equilibrium, the presence of H_2O in the initial mixture (as from a vitiated main stream) increased ignition times at initial temperatures below 1000 K and reduced ignition times by about 33 percent at temperatures above 1200 K. These results were found to be due to the depletion of H atoms by the accelerated production of HO_2 at low initial temperatures through the reaction $H + O_2 + H_2O \rightarrow HO_2 + H_2O$, because the third-body efficiency of H_2O may be 13 times that of N_2. At higher temperatures the dissociation of H_2O produces OH concentrations that counteract the H atom depletion and reduce ignition time. The presence of chemicals such as H_2O_2, O_3, NO, and NO_2, in concentrations (mass fractions) of 0.01 in both H_2-air and H_2-vitiated air mixtures, significantly reduced ignition times at low temperatures (near 910 K). At high temperatures (above 1100 K) NO and NO_2 had little effect on ignition times, whereas H_2O_2 and O_3 still caused a reduction of ignition times by about a factor of 7.

The present calculations indicate that reaction time, defined as the time from the onset of ignition to attainment of 95 percent of the equilibrium temperature, is independent of the concentration of free radicals, chemical additives, and within 10 percent, the equivalence ratio between 0.5 and 1.5. In addition, the presence of H_2O in a vitiated main stream at mass fractions of up to 0.245 had very little effect on reaction time. However, a comparison of rate constants for the reaction $H + OH + M \rightarrow H_2O + M$ indicates a need for more accurate rate data with N_2 and H_2O as third bodies.

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June 3, 1981

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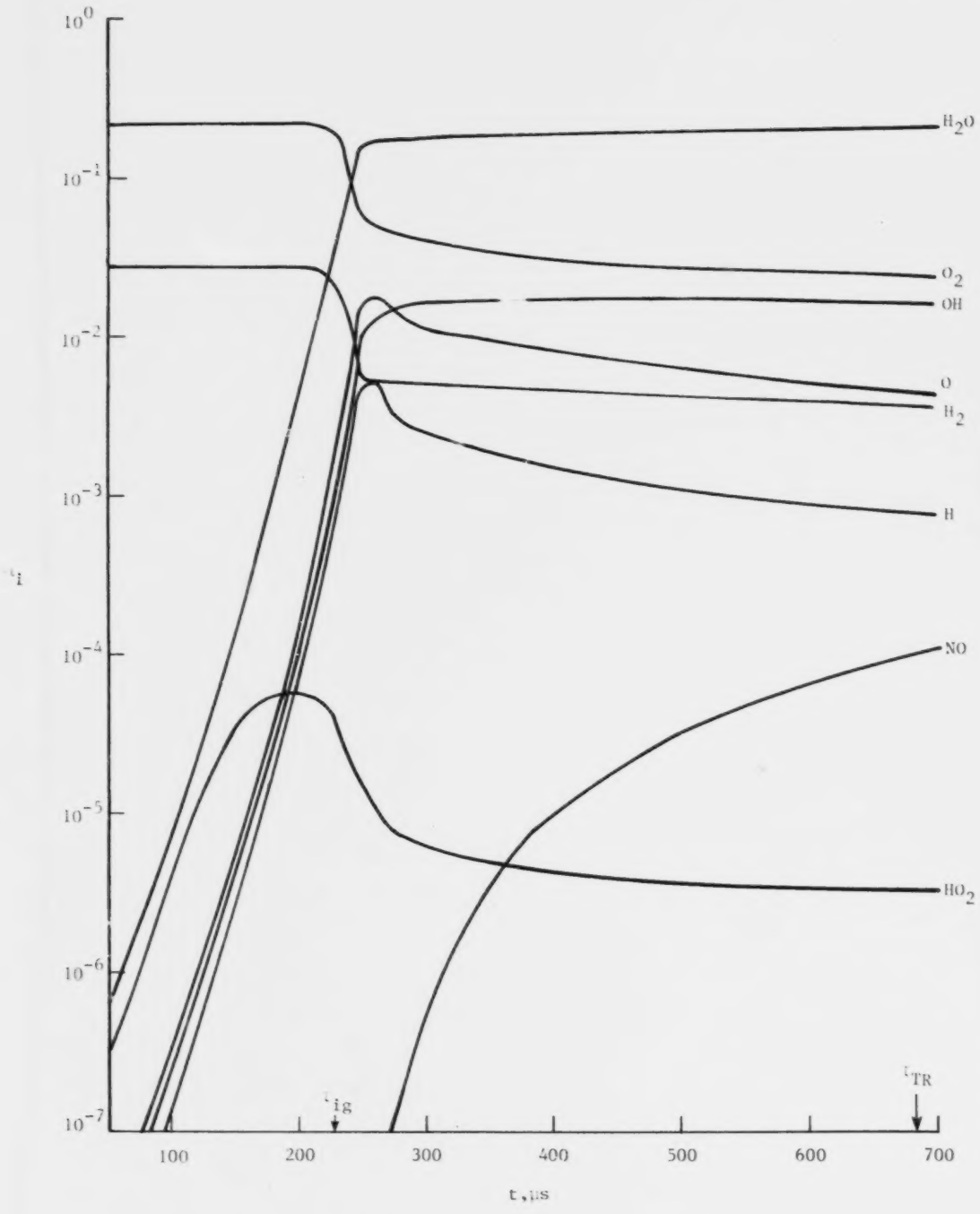
TABLE I.- HYDROGEN-AIR-REACTION MODEL WITH THIRD-BODY EFFICIENCIES

[Rate constant is given by $k = AT^N \exp(-\text{Activation energy}/1.987T)$]

REACTION NUMBER	REACTION	REACTION RATE VARIABLES A	N	ACTIVATION ENERGY
1	M + 1*O2 = 1*O + 1*O + M	.72000E+19	-1.0000	117908.00
2	M + 1*H2 = 1*H + 1*H + M	.55000E+19	-1.0000	103298.00
3	M + 1*H2O = 1*H + 1*OH + M	.52000E+22	-1.5000	119000.00
4	1*M + 1*O2 = 1*HO2 + M	.23000E+16	0.0000	-800.00
5	M + 1*NO2 = 1*NO + 1*O + M	.11000E+17	0.0000	66995.00
6	M + 1*NO = 1*N + 1*O + M	.41000E+19	-1.0000	149680.00
7	1*O + 1*CO = 1*CO2 + M	.30000E+15	0.0000	3000.00
8	1*H + 1*NO = 1*HNO + M	.54000E+16	0.0000	-596.10
9	M + 1*H2O2 = 1*OH + 1*OH + M	.12000E+18	0.0000	45500.00
10	1*OH + 1*NO = 1*HNO2 + M	.80000E+16	0.0000	-1987.00
11	1*OH + 1*NO2 = 1*HNO3 + M	.13000E+17	0.0000	-2200.00
12	M + 1*O3 = 1*O2 + 1*O + M	.13000E+22	-2.0000	25433.00
13	M + 1*HCO = 1*CO + 1*H + M	.20000E+13	.5000	27400.00
14	1*O + 1*H = 1*OH + M	.71000E+19	-1.0000	0.00
15	1*H2O + 1*O = 1*OH + 1*OH	.58000E+14	0.0000	18000.00
16	1*H2 + 1*OH = 1*H2O + 1*H	.20000E+14	0.0000	5166.00
17	1*O2 + 1*H = 1*OH + 1*O	.22000E+15	0.0000	16800.00
18	1*H2 + 1*O = 1*OH + 1*H	.75000E+14	0.0000	11099.00
19	1*H2 + 1*O2 = 1*OH + 1*OH	.10000E+14	0.0000	43000.00
20	1*H + 1*HO2 = 1*H2 + 1*O2	.24000E+14	0.0000	695.00
21	1*H2 + 1*O2 = 1*H2O + 1*O	.41000E+14	0.0000	50470.00
22	1*H + 1*HO2 = 1*OH + 1*OH	.24000E+15	0.0000	1987.00
23	1*H2O + 1*O = 1*H + 1*HO2	.58000E+12	.5000	57000.00
24	1*O + 1*HO2 = 1*OH + 1*O2	.50000E+14	0.0000	1000.00
25	1*OH + 1*HO2 = 1*O2 + 1*H2O	.30000E+14	0.0000	0.00
26	1*H2 + 1*HO2 = 1*H2O + 1*OH	.20000E+14	0.0000	25000.00
27	1*HO2 + 1*H2 = 1*H + 1*H2O2	.73000E+12	0.0000	18677.00
28	1*H2O2 + 1*H = 1*OH + 1*H2O	.32000E+15	0.0000	4980.00
29	1*HO2 + 1*OH = 1*O + 1*H2O2	.52000E+11	.5000	21062.00
30	1*HO2 + 1*H2O = 1*OH + 1*H2O2	.28000E+14	0.0000	32785.00
31	1*HO2 + 1*HO2 = 1*H2O2 + 1*O2	.20000E+13	0.0000	0.00
32	1*O + 1*O3 = 1*O2 + 1*O2	.10000E+14	0.0000	4790.00
33	1*O3 + 1*NO = 1*NO2 + 1*O2	.54000E+12	0.0000	2384.00
34	1*O3 + 1*H = 1*OH + 1*O2	.70000E+14	0.0000	1113.00
35	1*O3 + 1*OH = 1*O2 + 1*HO2	.90000E+12	0.0000	1987.00
36	1*O + 1*N2 = 1*NO + 1*N	.50000E+14	0.0000	75386.00
37	1*H + 1*NO = 1*OH + 1*N	.17000E+15	0.0000	48681.00
38	1*O + 1*NO = 1*O2 + 1*N	.15000E+10	1.0000	38746.00
39	1*NO2 + 1*H = 1*NO + 1*OH	.35000E+15	0.0000	1470.00
40	1*NO2 + 1*O = 1*NO + 1*O2	.10000E+14	0.0000	600.00
41	1*NO2 + 1*H2 = 1*HNO2 + 1*H	.24000E+14	0.0000	29000.00
42	1*HO2 + 1*NO = 1*NO2 + 1*OH	.30000E+13	.5000	2400.00
43	1*NO2 + 1*H2O = 1*HNO2 + 1*OH	.32000E+13	0.0000	43714.00
44	1*NO2 + 1*OH = 1*HNO2 + 1*O	.21000E+13	0.0000	24990.00
45	1*CO + 1*OH = 1*CO2 + 1*H	.70000E+12	0.0000	1987.00
46	1*CO2 + 1*O = 1*O2 + 1*CO	.25000E+12	.5000	55040.00
47	1*H2O + 1*CO = 1*HCO + 1*OH	.65000E+14	.3000	103026.00
48	1*OH + 1*CO = 1*HCO + 1*O	.58000E+13	.3200	86295.00
49	1*H2 + 1*CO = 1*HCO + 1*H	.12000E+14	.2900	89242.00
50	1*HO2 + 1*CO = 1*CO2 + 1*OH	.15000E+15	0.0000	23645.00
51	1*HNO + 1*H = 1*H2 + 1*NO	.48000E+13	0.0000	0.00
52	1*HNO + 1*OH = 1*H2O + 1*NO	.36000E+14	0.0000	0.00
53	1*NO + 1*CO = 1*CO2 + 1*N	.46000E+09	.5000	21981.00
54	1*NO2 + 1*CO = 1*NO + 1*CO2	.10000E+13	0.0000	27600.00
55	1*NO + 1*HO2 = 1*HNO + 1*O2	.72000E+11	.5000	10928.00
56	1*HNO + 1*O = 1*NO + 1*OH	.50000E+12	.5000	0.00
57	1*HNO3 + 1*O = 1*HO2 + 1*NO2	.10000E+12	0.0000	0.00
58	1*HO2 + 1*NO2 = 1*HNO2 + 1*O2	.20000E+12	0.0000	0.00
59	1*HCO + 1*O2 = 1*CO + 1*HO2	.10000E+12	.5000	5400.00
60	1*O3 + 1*HO2 = 2*O2 + 1*OH	.10000E+12	0.0000	2400.00

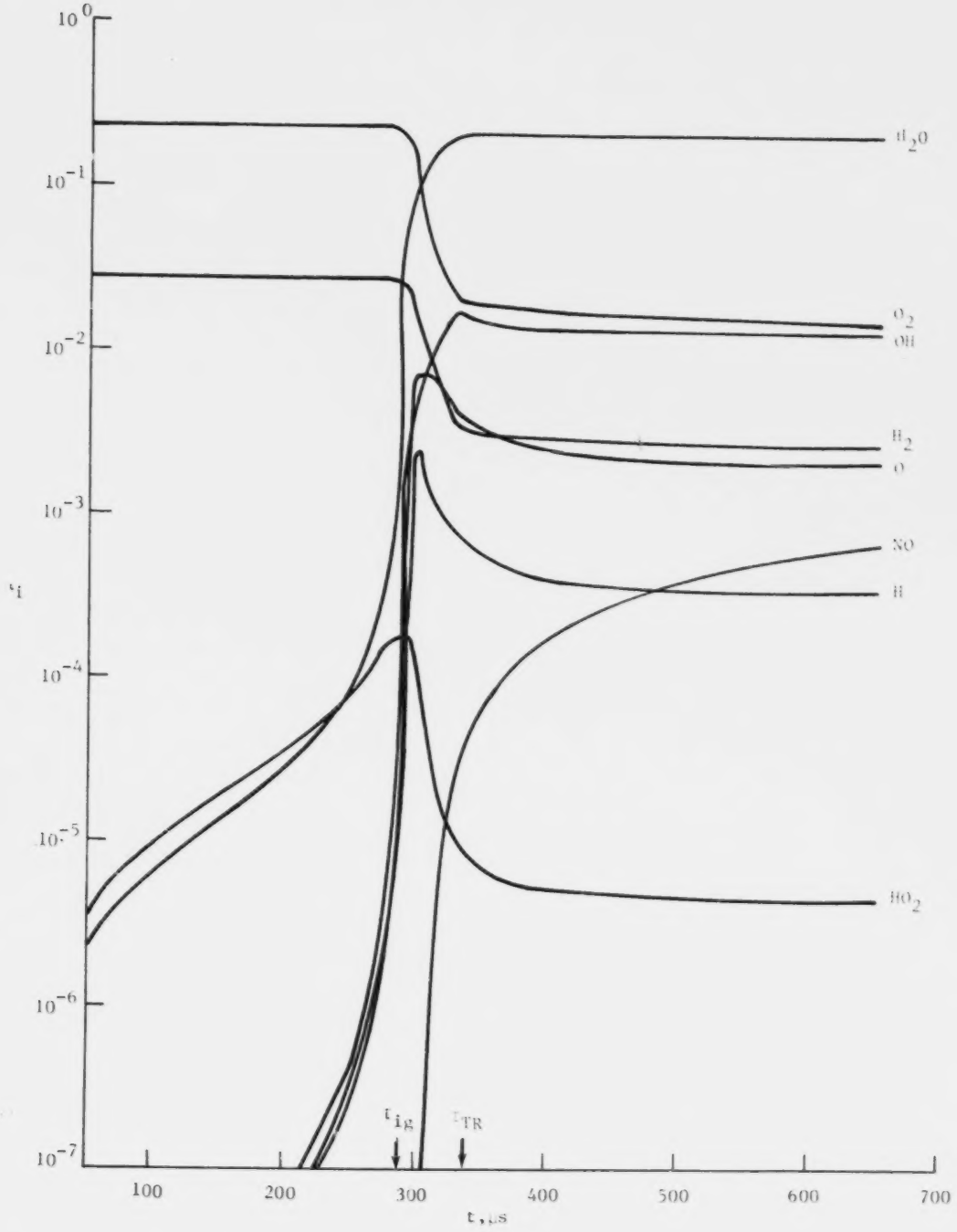
ALL THIRD BODY RATIOS ARE 1.0 EXCEPT THE FOLLOWING

M(O2 , 1) =	4.00000	M(O2 , 12) =	1.50000	M(O , 1) =	10.00000	M(H2 , 2) =	2.00000
M(H2 , 4) =	2.00000	M(H , 2) =	5.00000	M(H2O , 1) =	2.00000	M(H2O , 2) =	8.00000
M(H2O , 3) =	6.00000	M(H2O , 4) =	13.00000	M(H2O , 8) =	3.00000	M(H2O , 9) =	5.00000



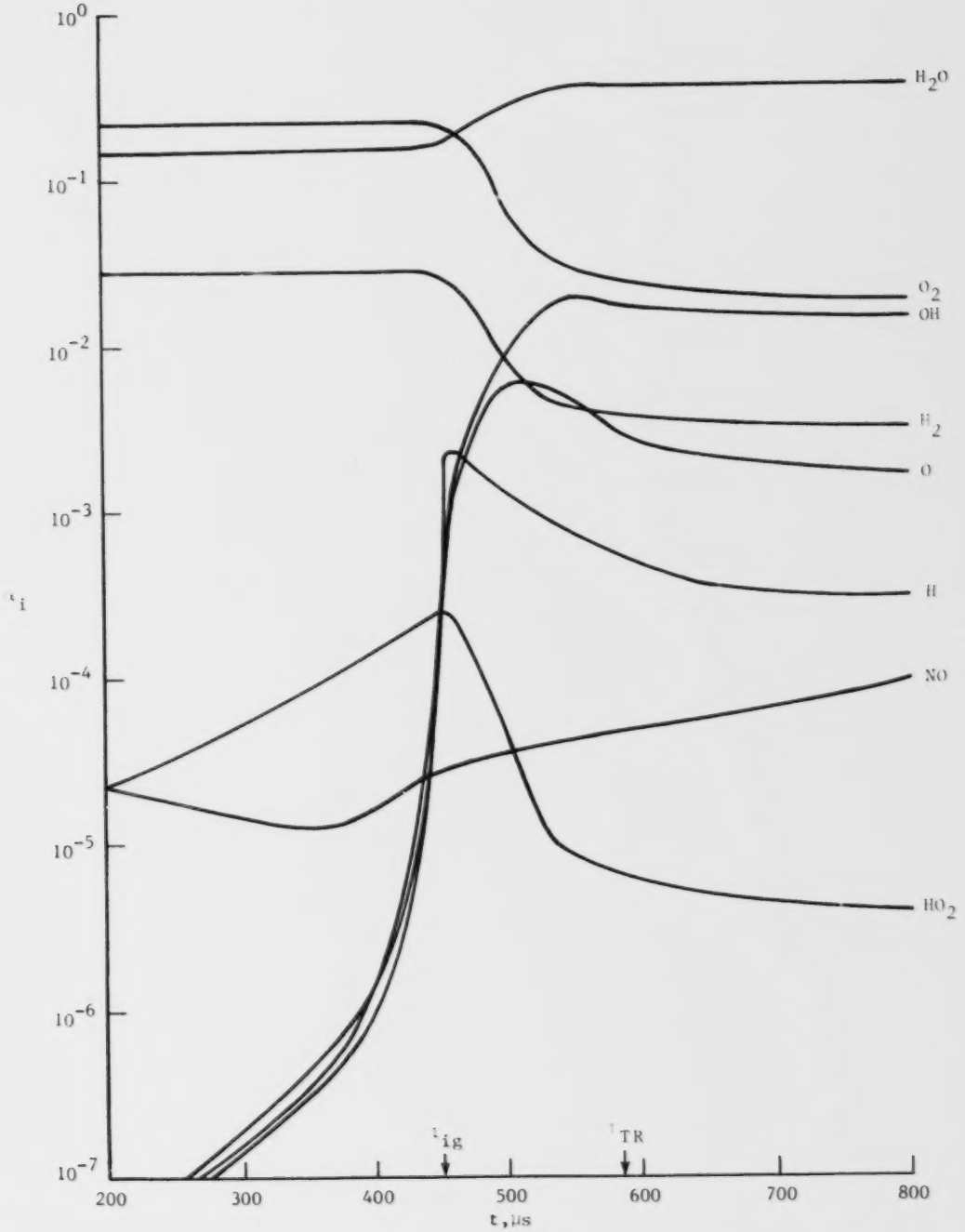
(a) H_2-air; p = 0.5 atm.

Figure 1.- Species mass fraction as function of time. ϕ = 1.0; T_o = 1000 K.



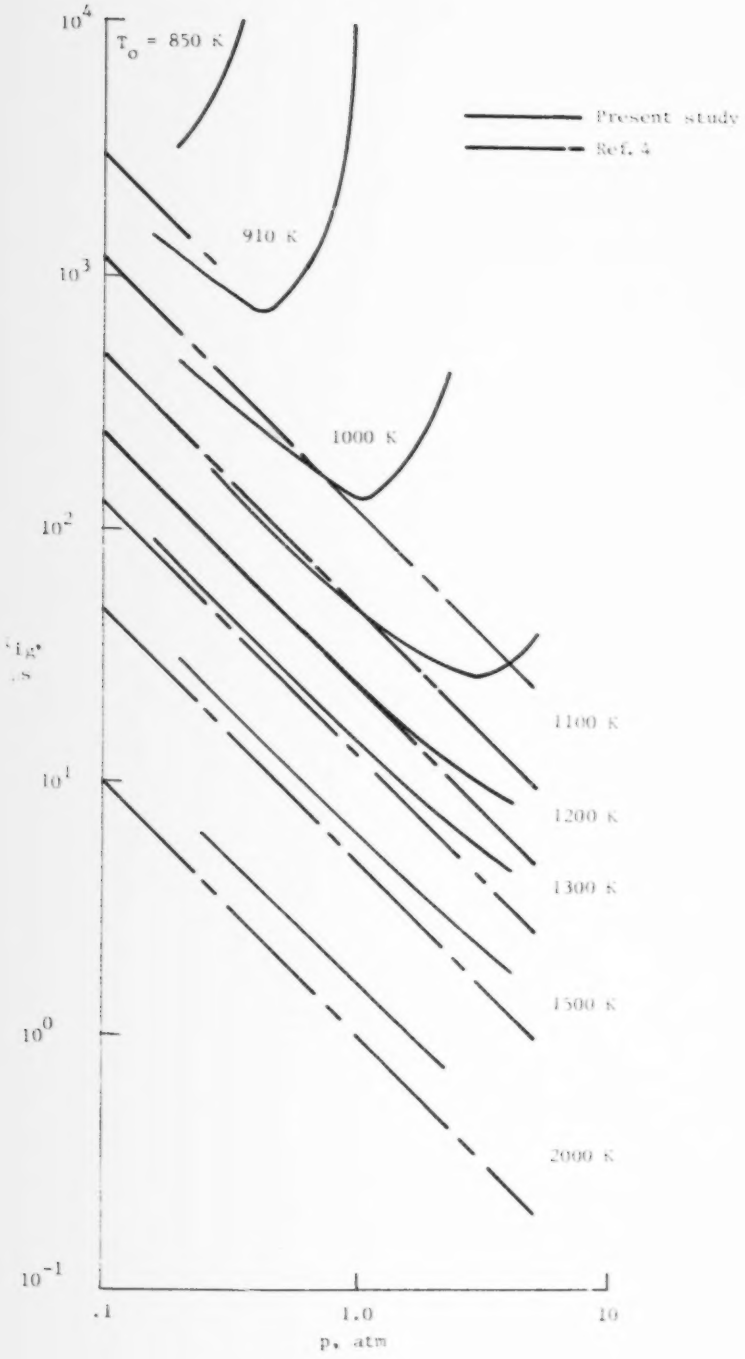
(b) H_2-air; p = 2.0 atm.

Figure 1.- Continued.



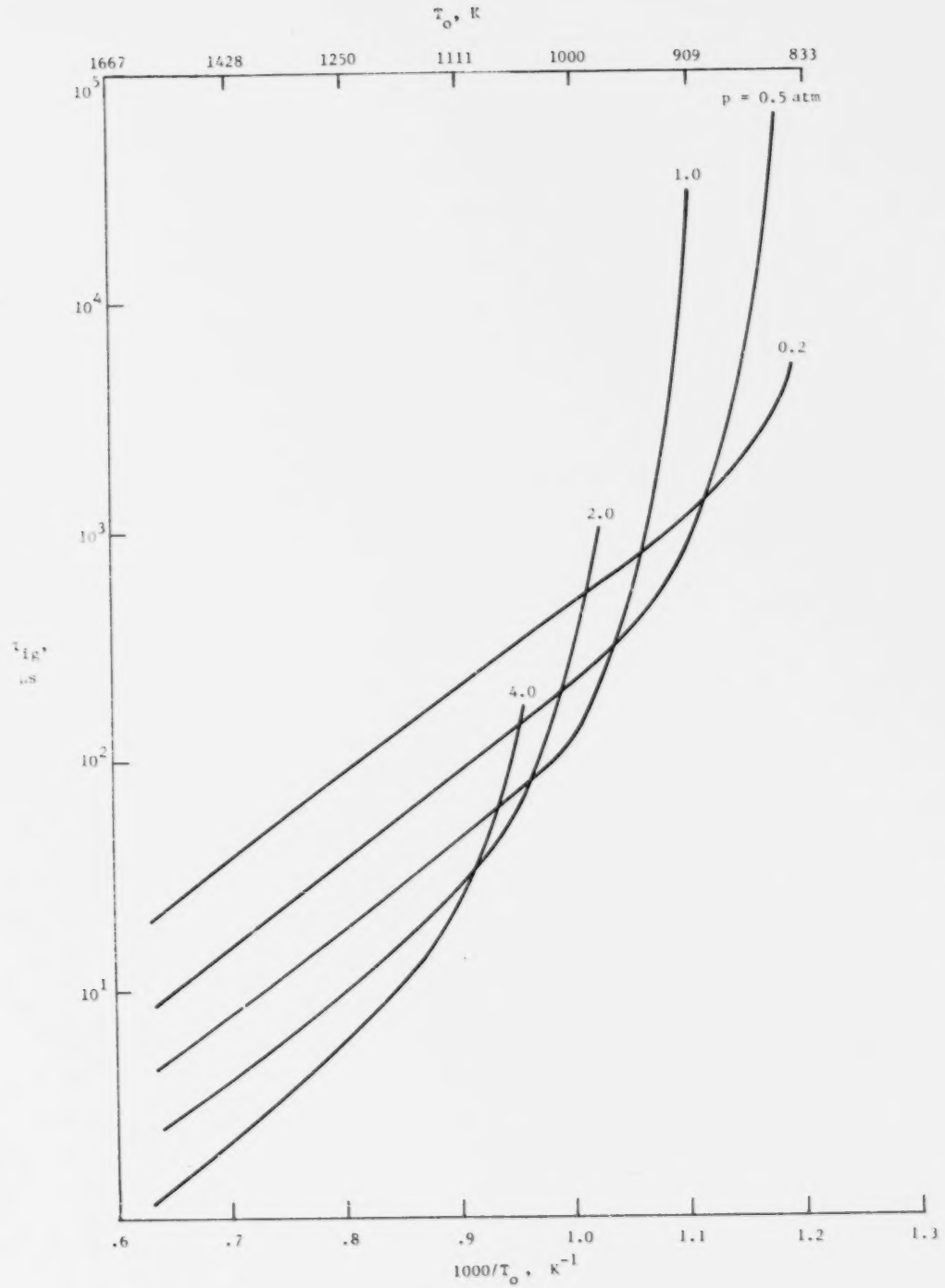
(c) H_2-vitiated air; p = 1.0 atm.

Figure 1.- Concluded.



(a) Effect of pressure.

Figure 2.- Theoretical ignition times for H_2-air.



(b) Effect of temperature.

Figure 2.- Concluded.

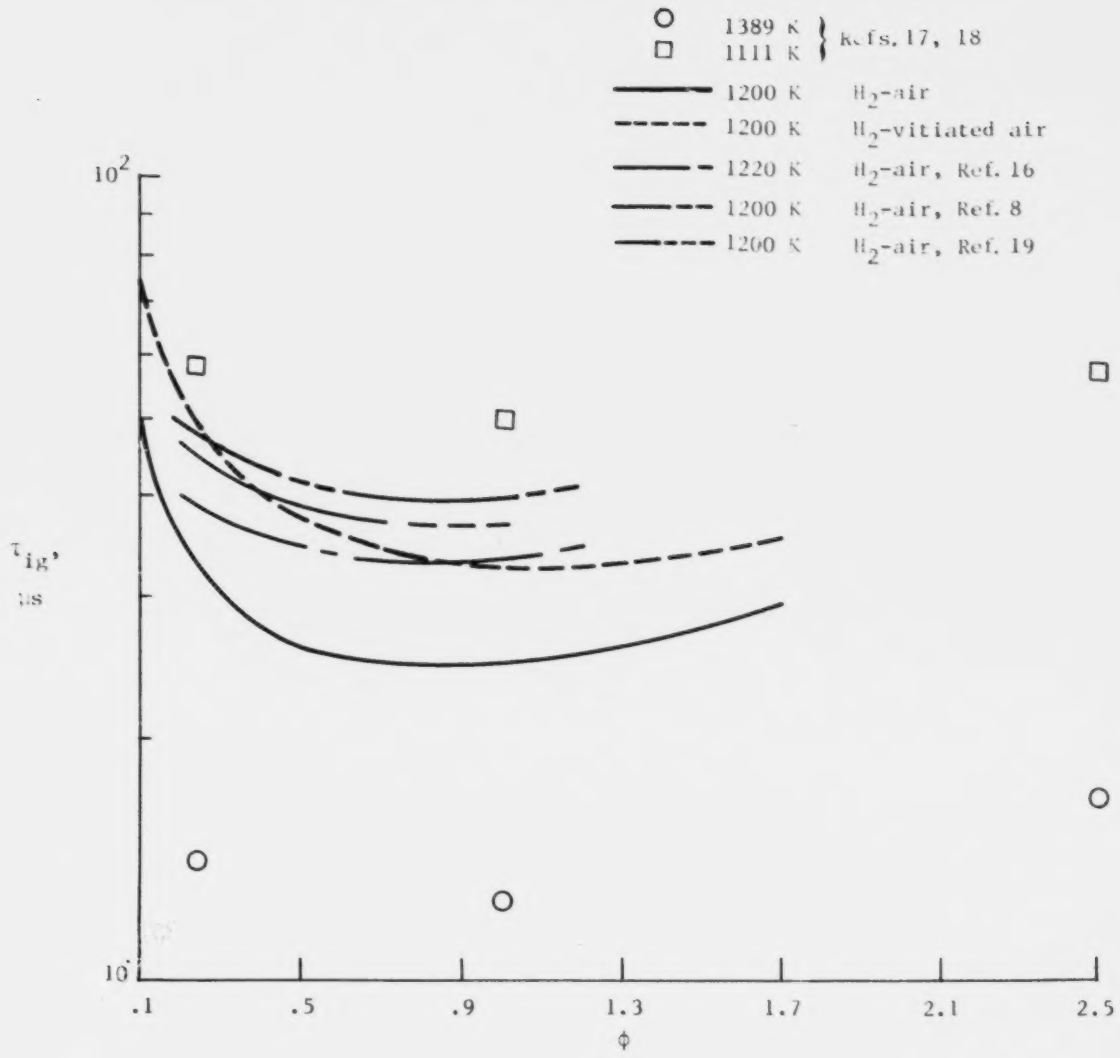
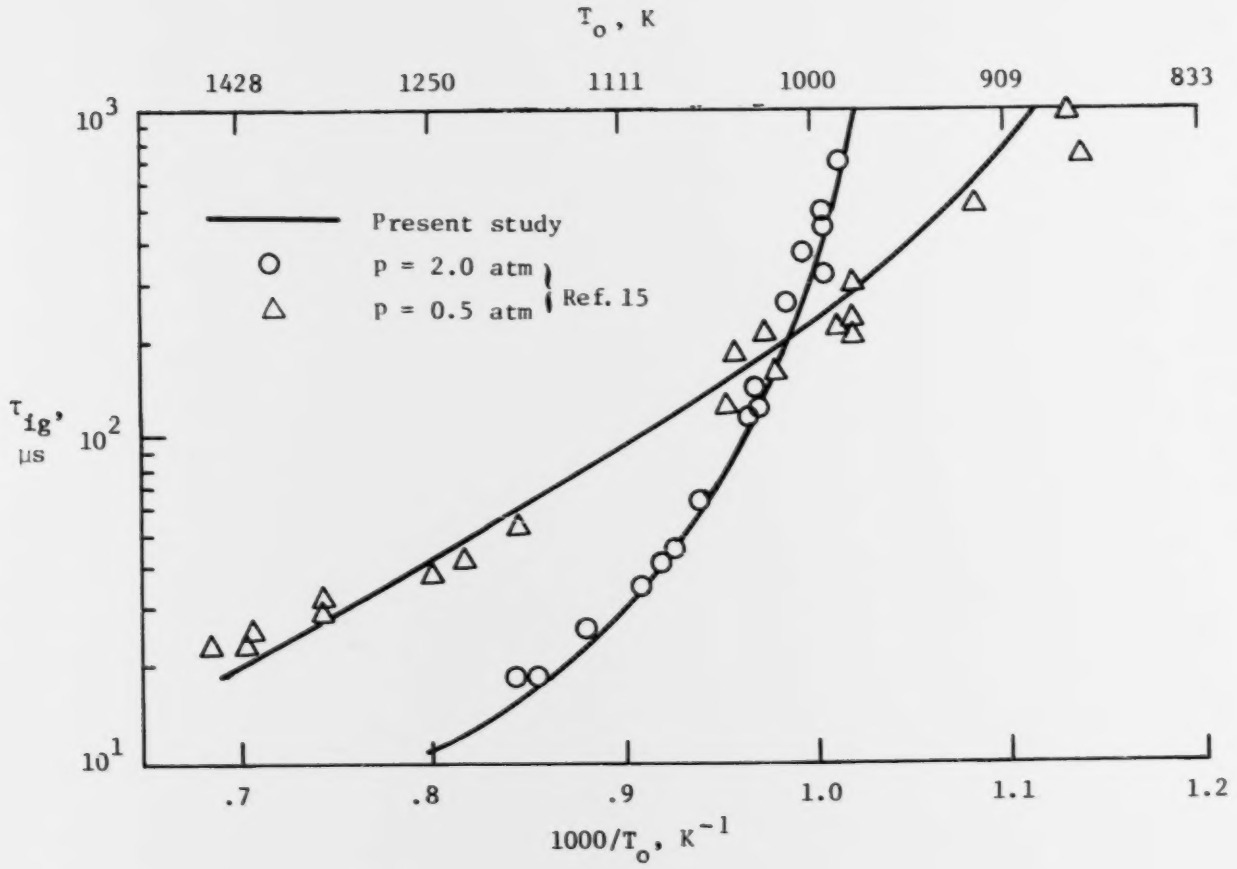
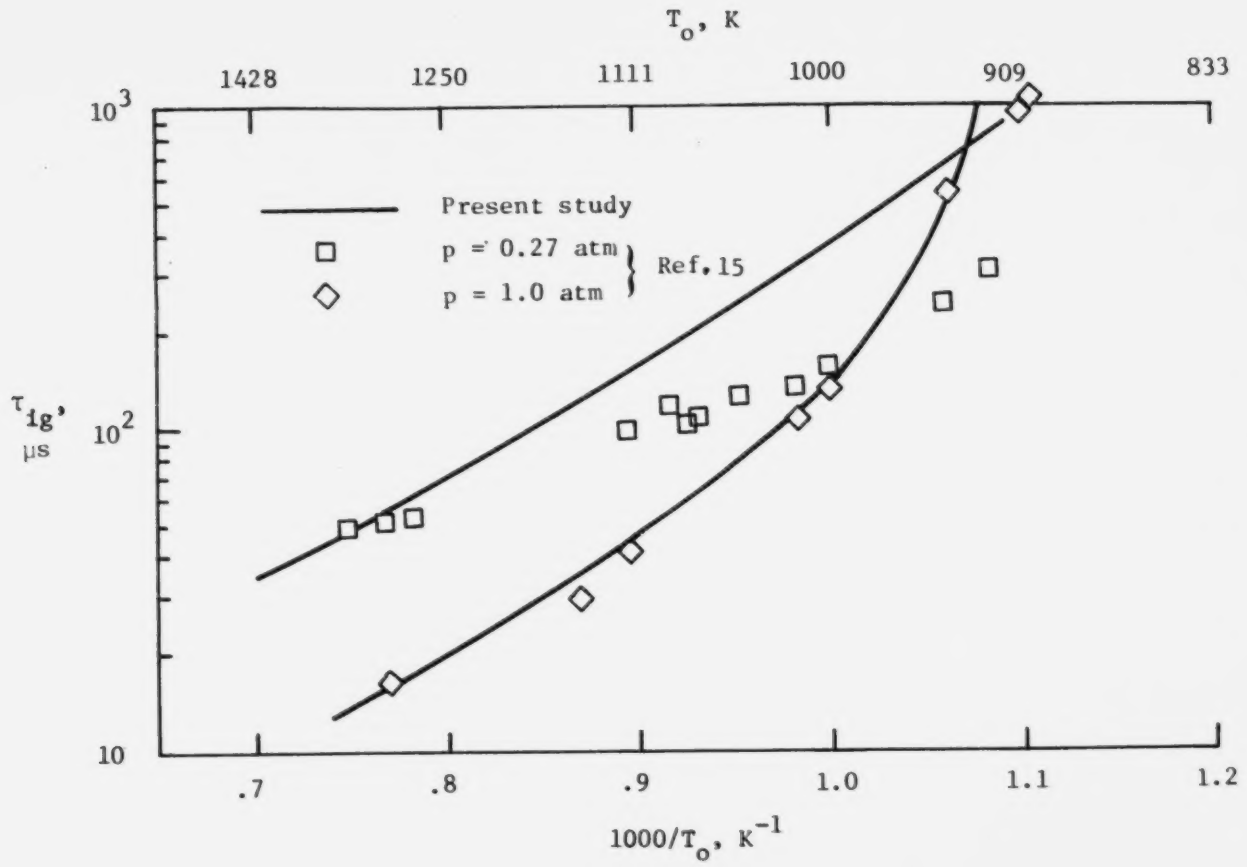


Figure 3.- Effect of equivalence ratio on ignition time. p = 1 atm.



(a) p = 0.5 and 2.0 atm.

Figure 4.- Ignition times for H_2-air. ϕ = 1.0.



(b) p = 0.27 and 1.0 atm.

Figure 4.- Concluded.

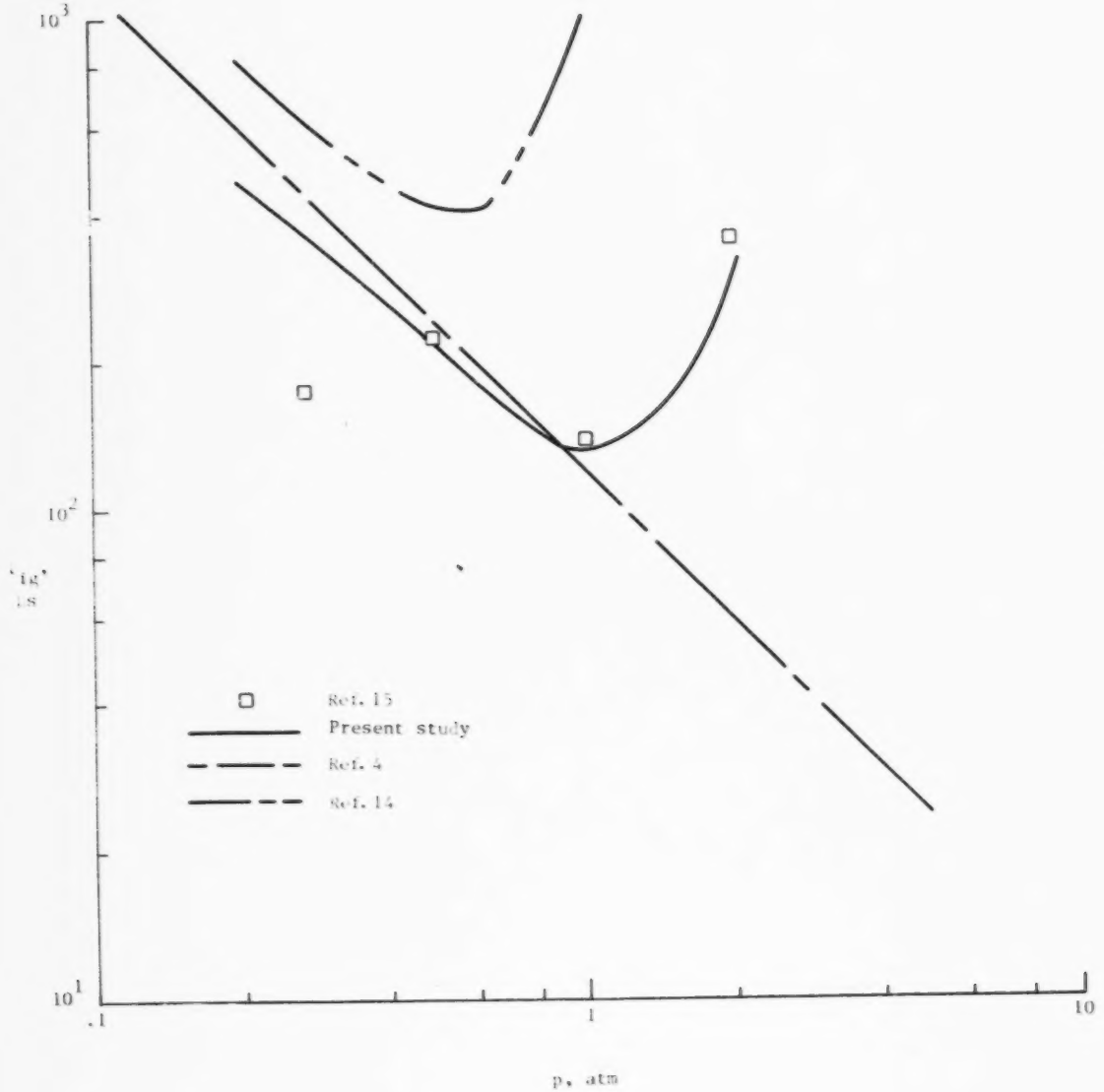
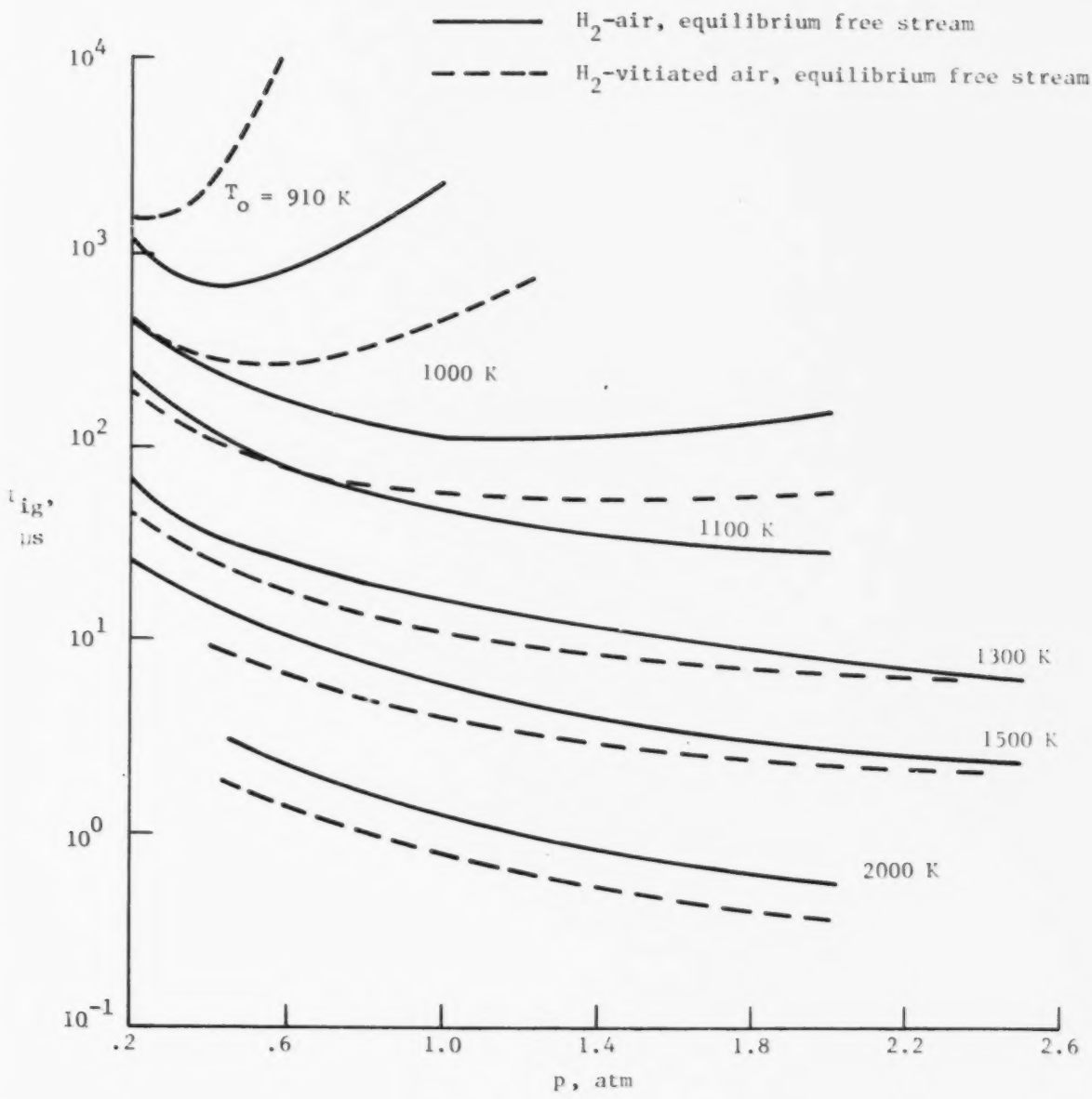
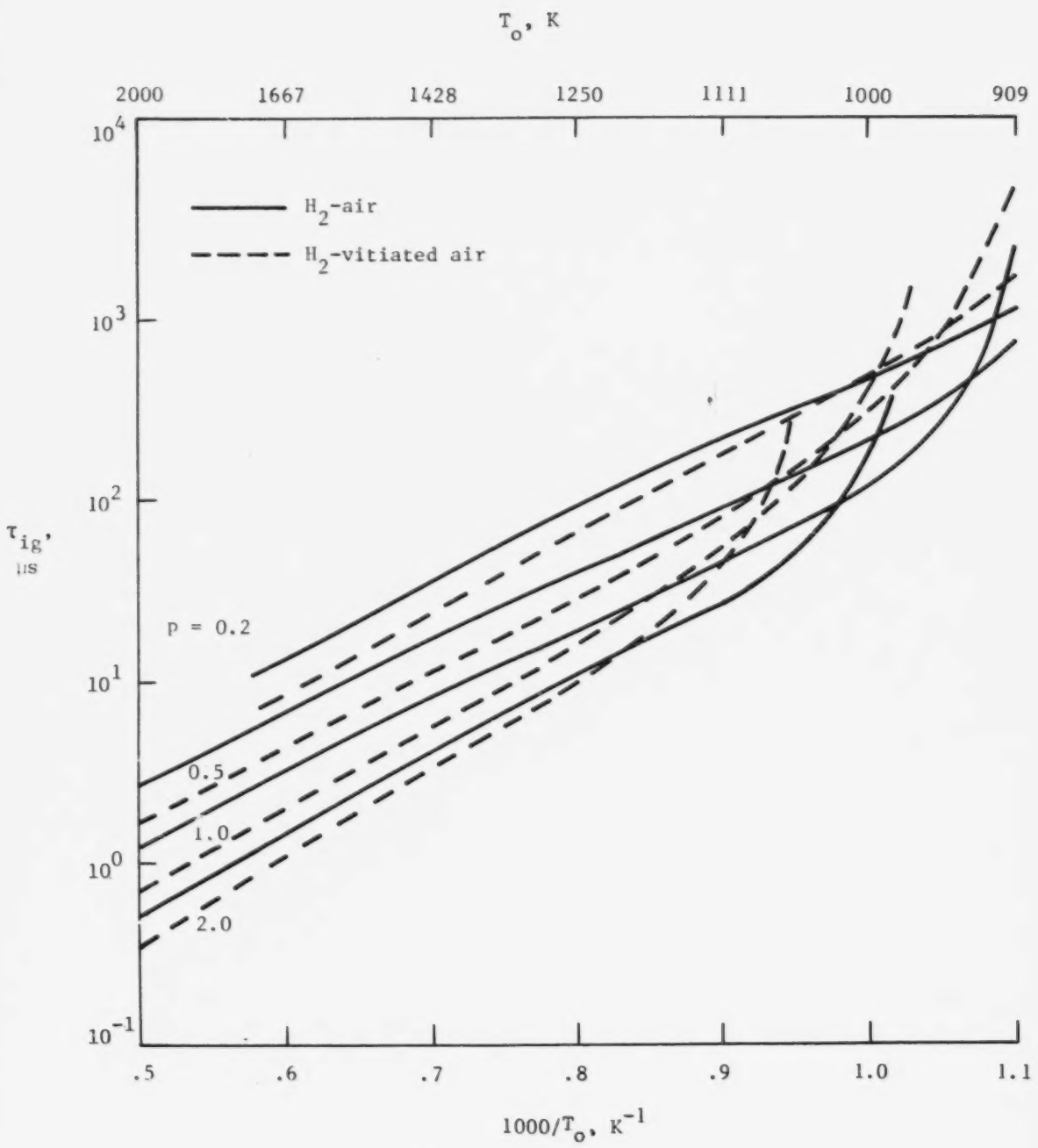


Figure 5.- Ignition times for H_2-air as function of pressure. T_o = 1000 K; ϕ = 1.0.



(a) Effect of pressure.

Figure 6.- Comparison of ignition times for H_2-air and H_2-vitiated air.



(b) Effect of temperature.

Figure 6.- Concluded.

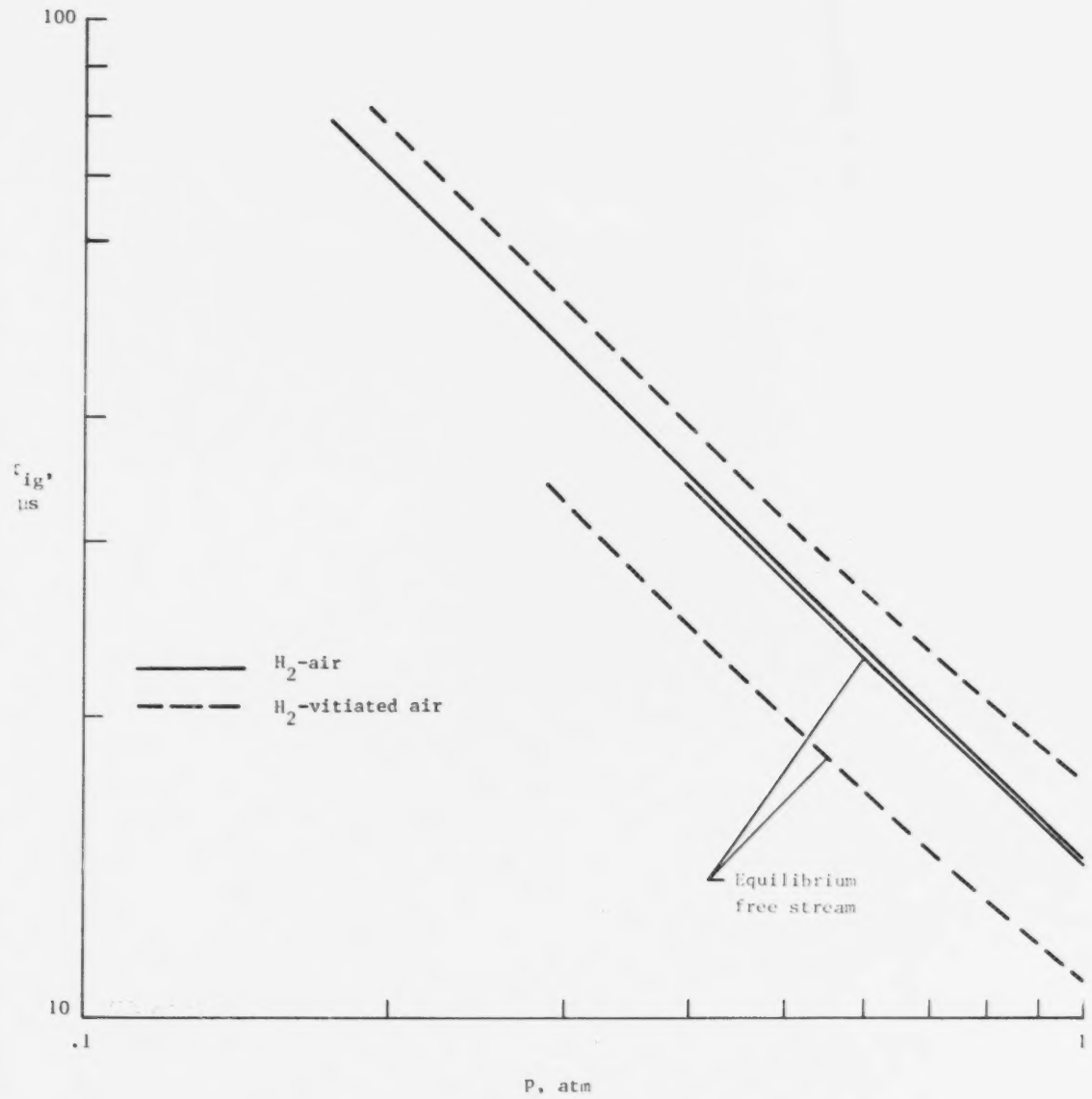


Figure 7.- Effect of equilibrium free stream on ignition times. T_o = 1300 K; ϕ = 1.0.

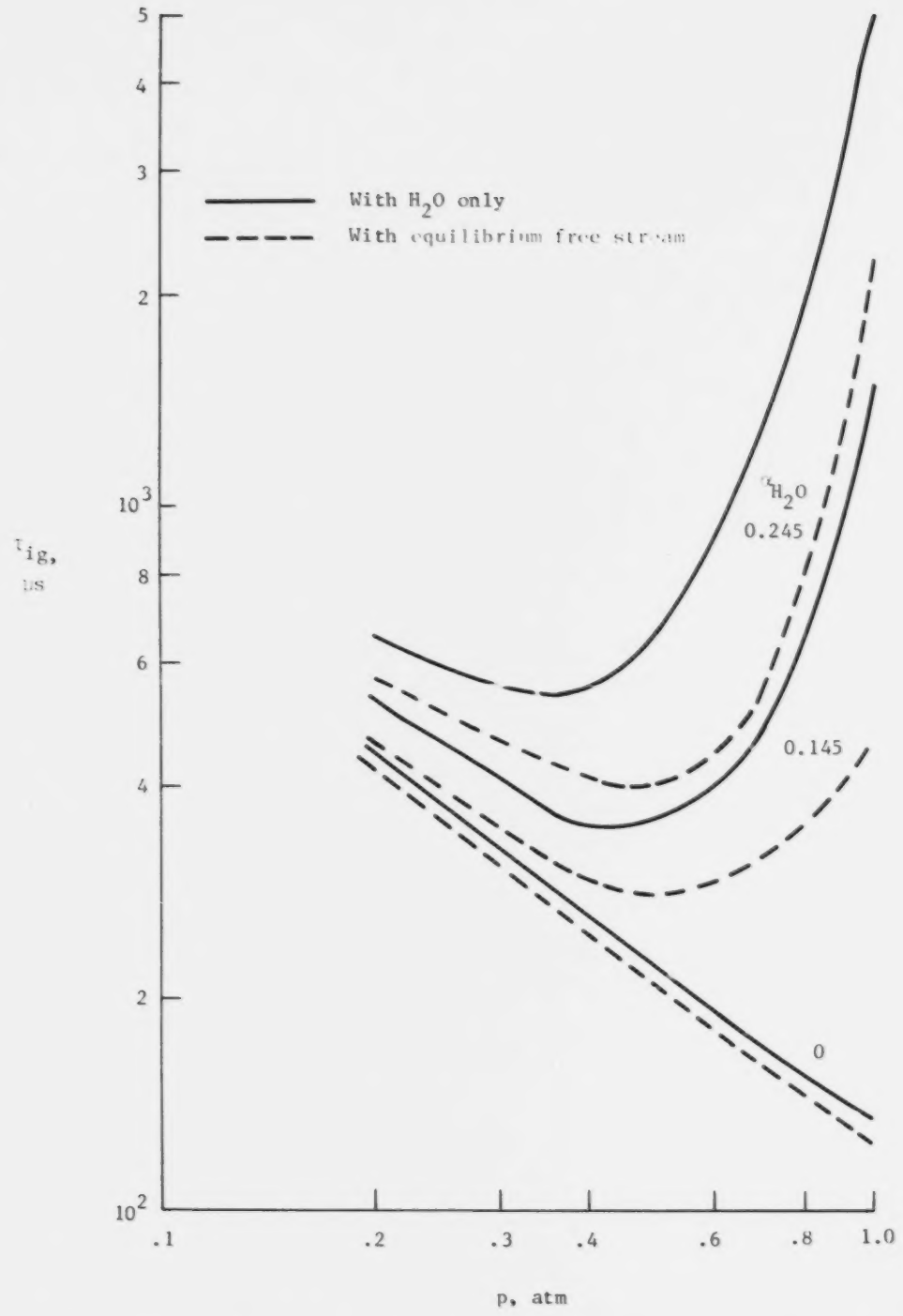


Figure 8.- Effect of H_2O concentration in test stream on ignition times. T_o = 1000 K.

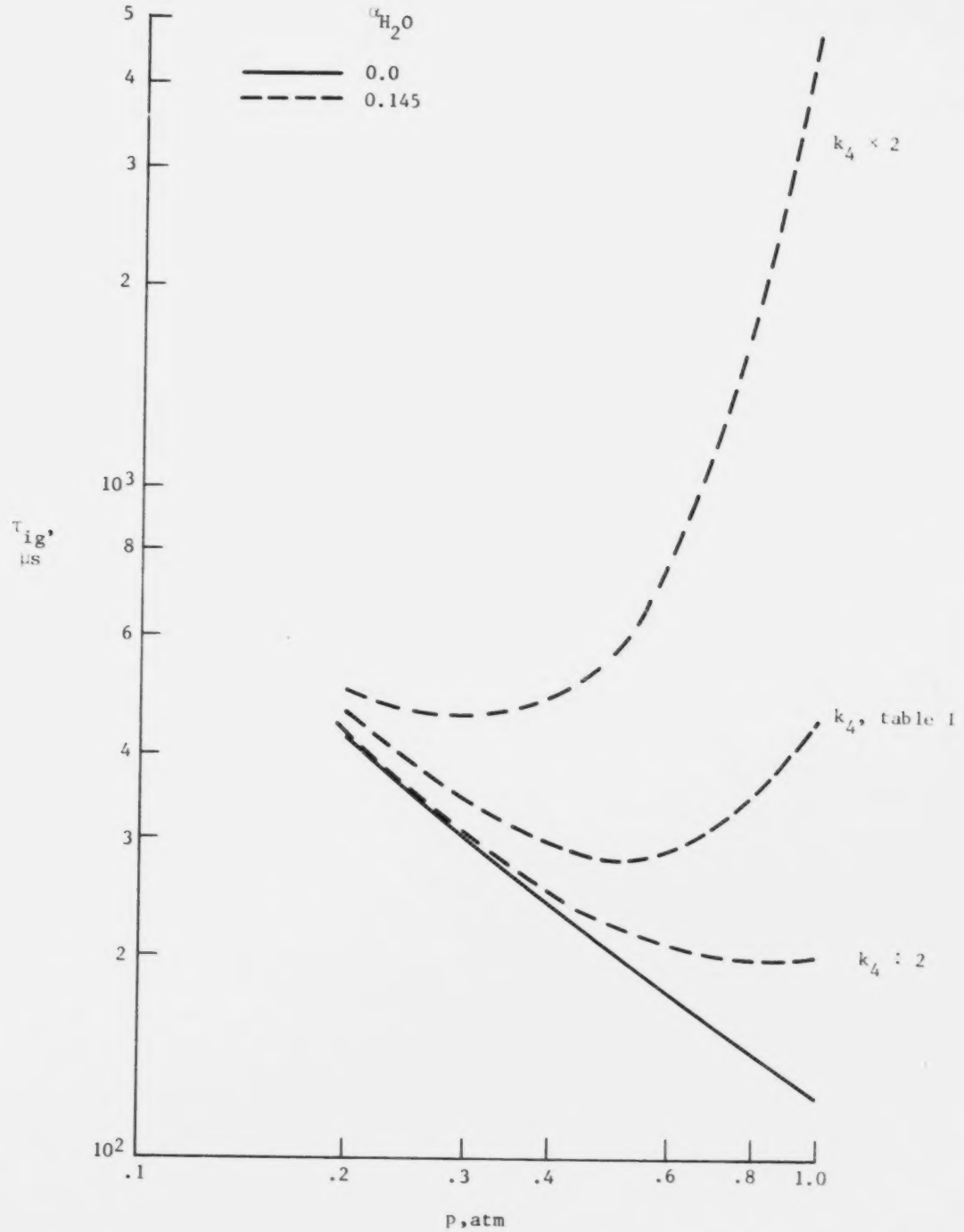
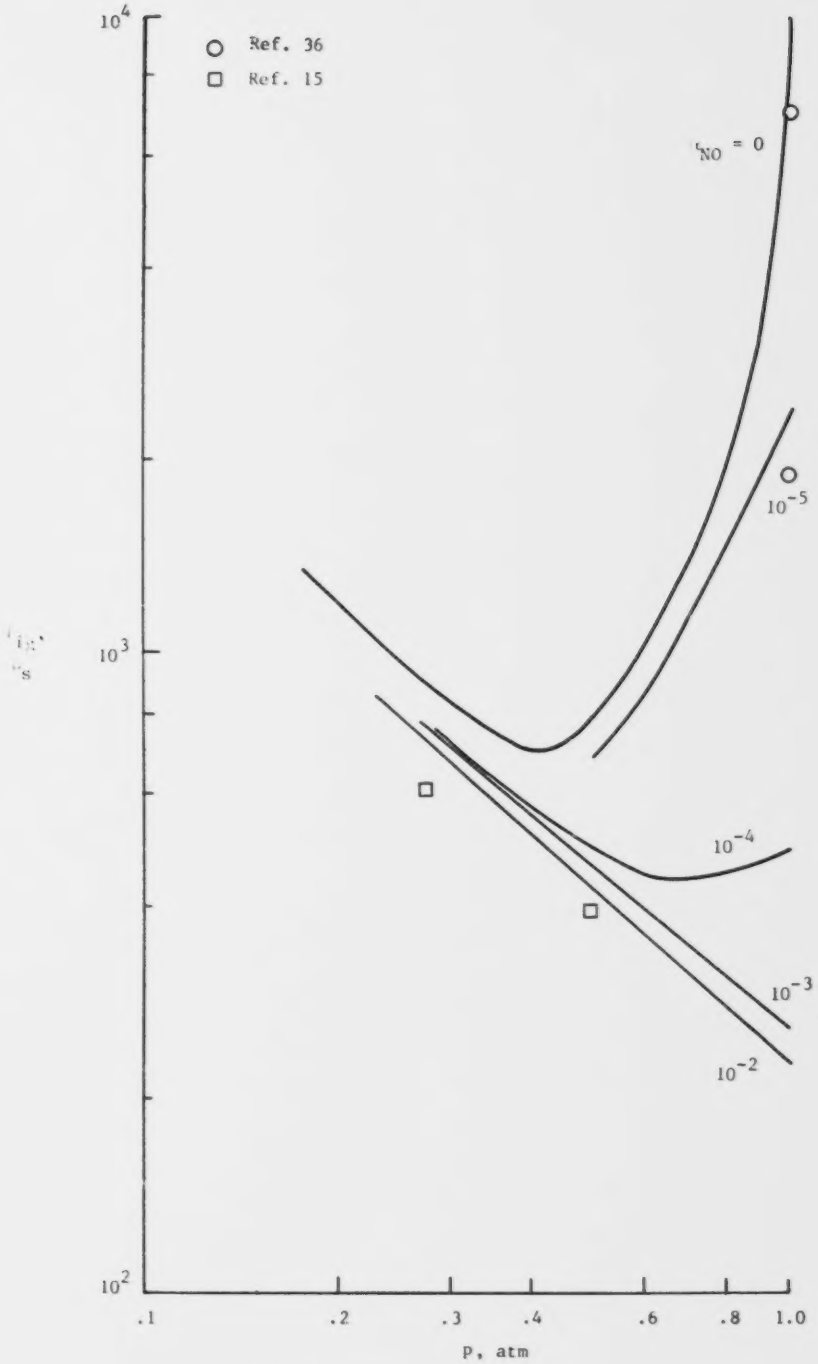
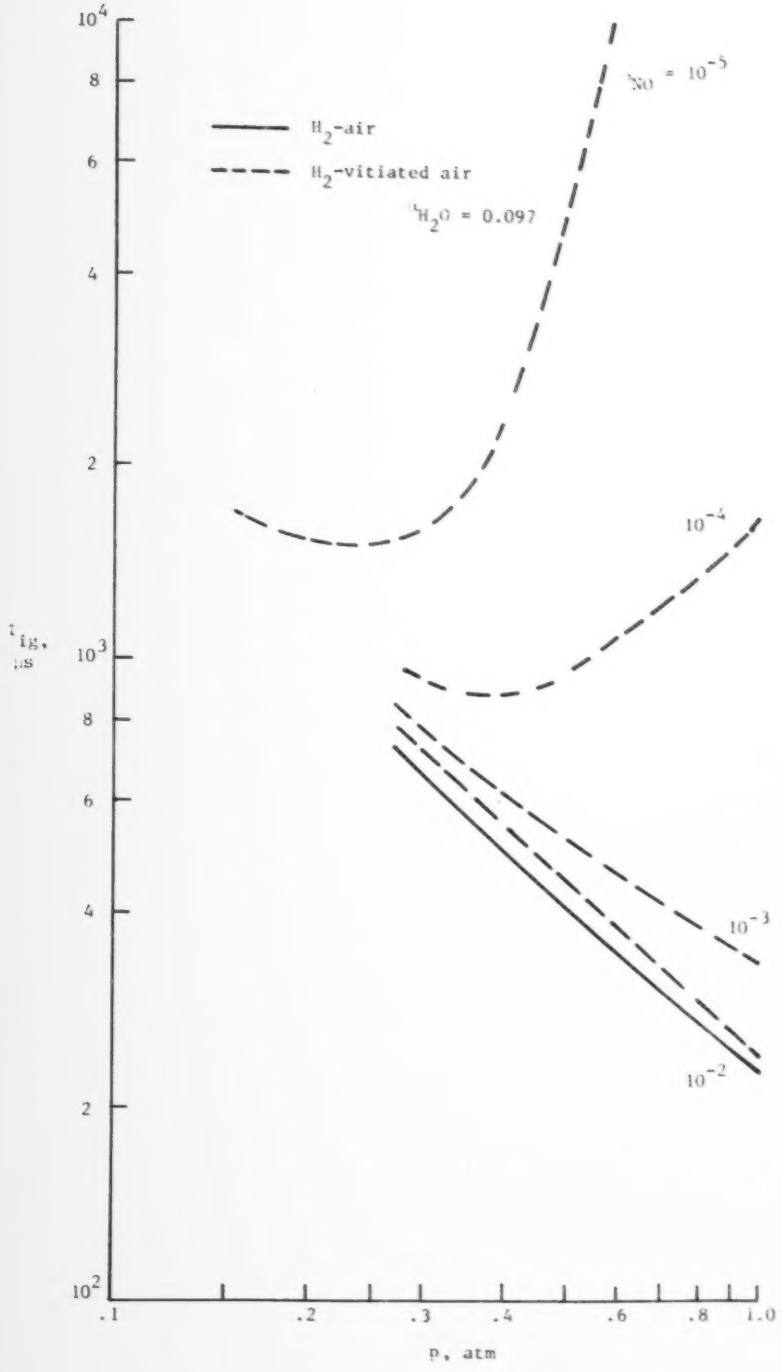


Figure 9.- Effect of rate constants for $H + O_2 + H_2O \rightarrow HO_2 + H_2O$ on ignition times in an H_2-vitiated air equilibrium free stream. $T_o = 1000$ K.



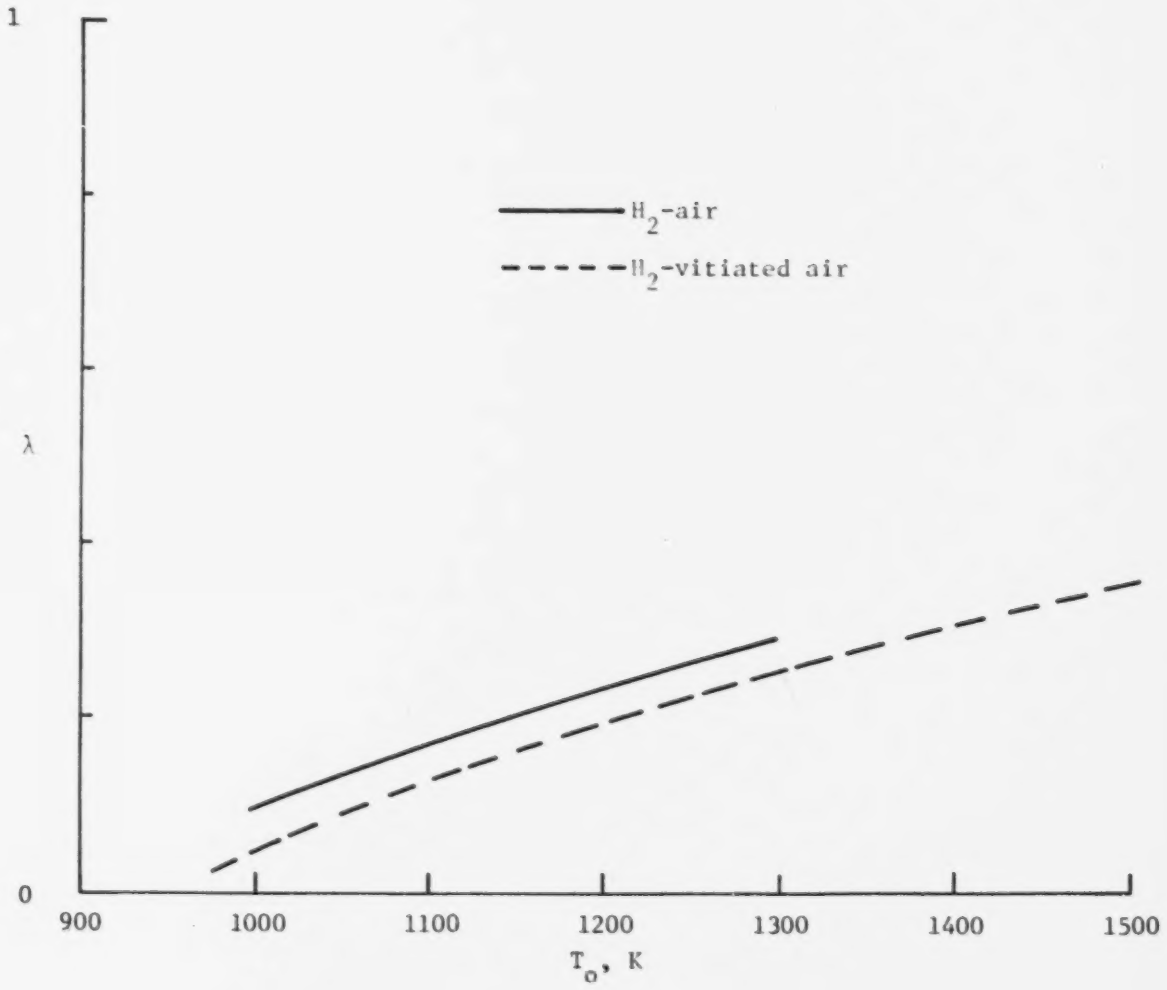
(a) H_2-air; T_o = 910 K.

Figure 10.- Effect of NO concentration on ignition times.



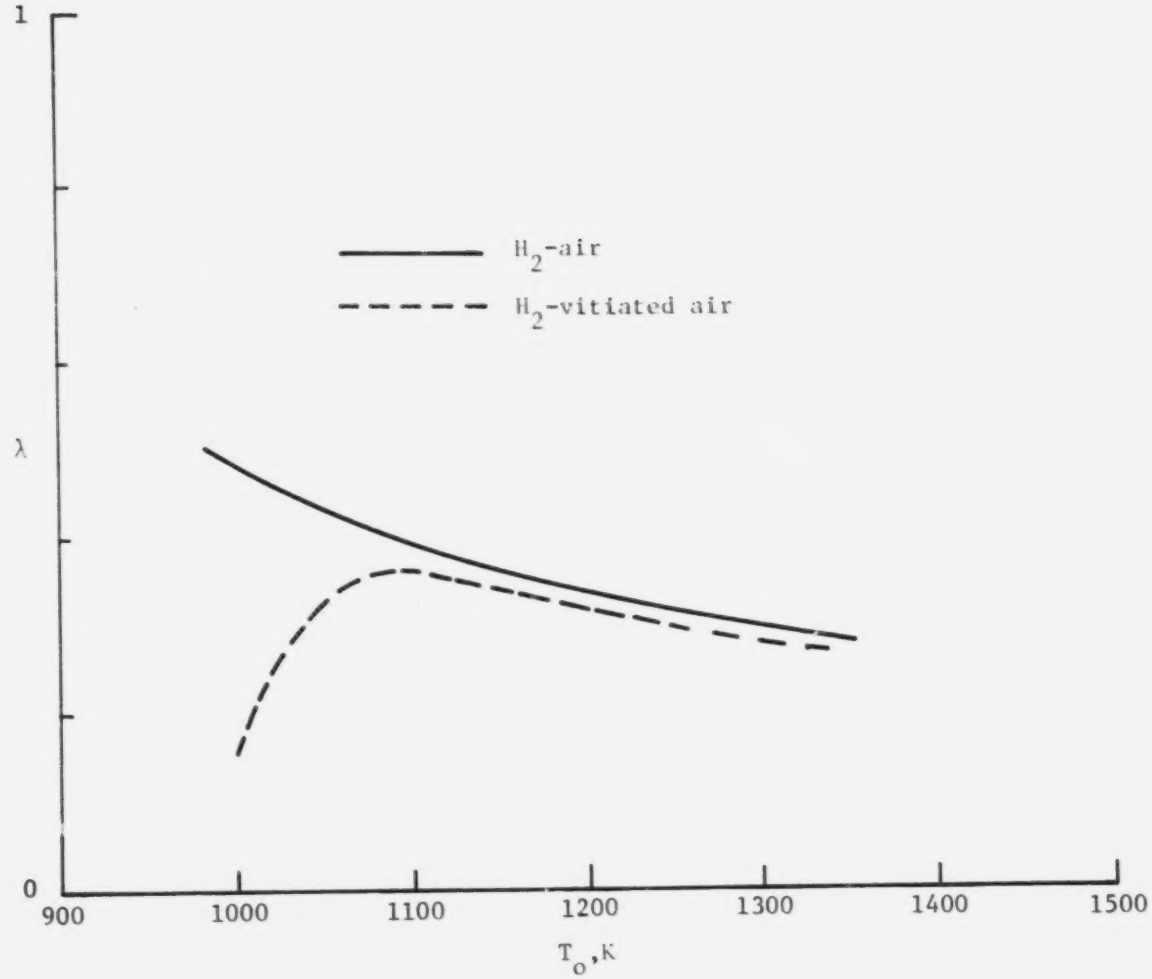
(b) H_2-vitiated air; T_o = 910 K.

Figure 10.- Concluded.



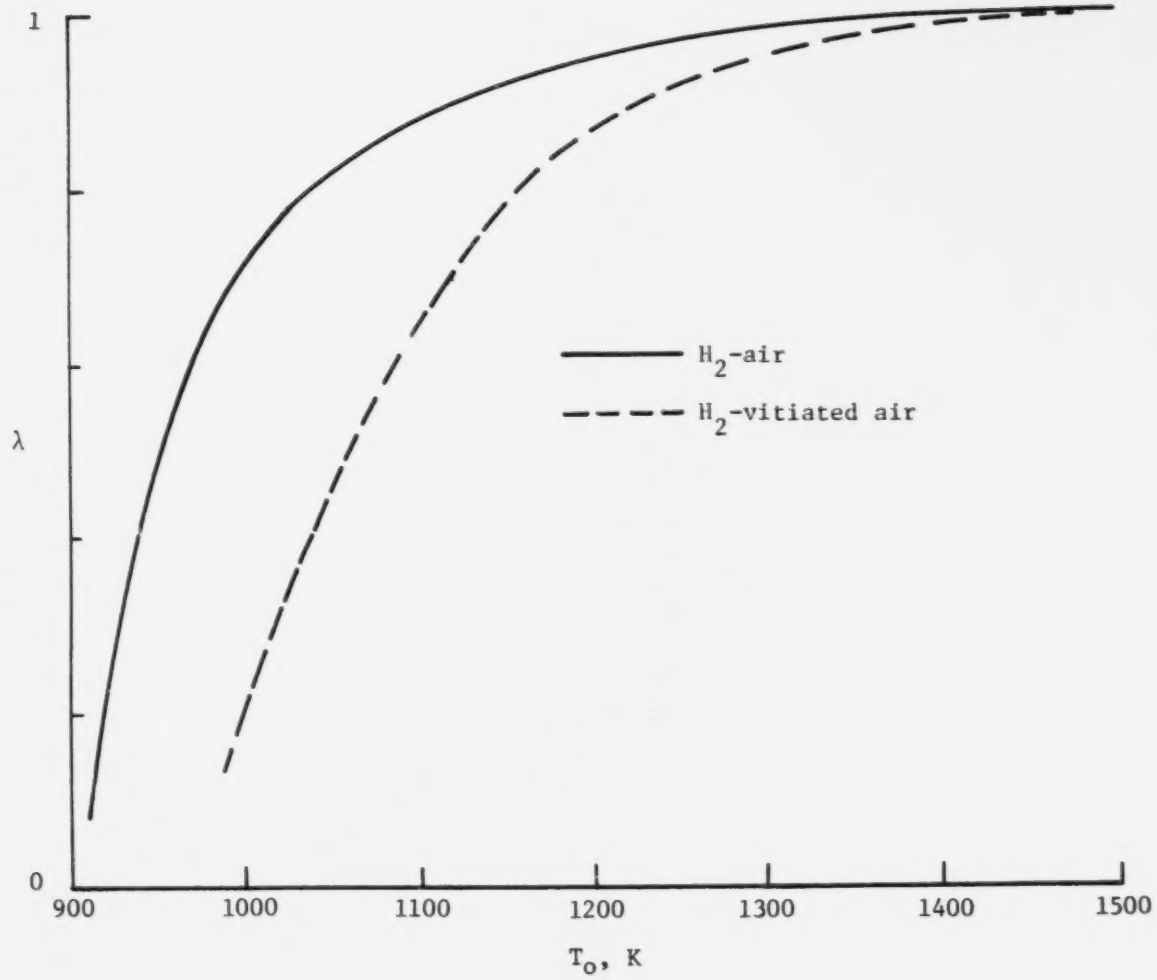
(a) $\alpha_{O_3} = 0.01$.

Figure 11.- Reduction of ignition times due to chemical additives. p = 1.0 atm; ϕ = 1.0.



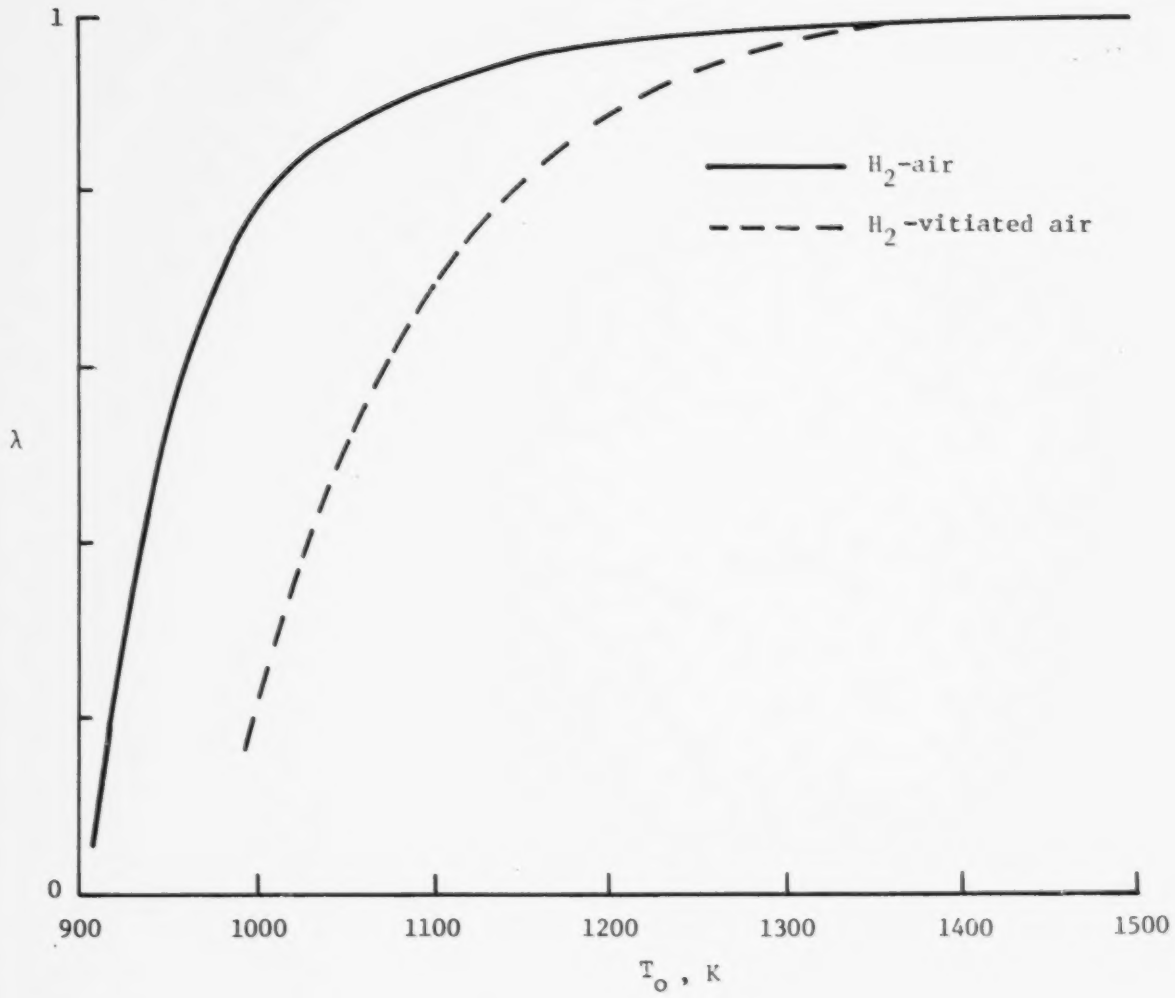
(b) $\alpha_{H_2O_2} = 0.01$.

Figure 11.- Continued.



(c) $\alpha_{NO} = 0.01$.

Figure 11.- Continued.



(d) $\alpha_{NO_2} = 0.01$.

Figure 11.- Concluded.

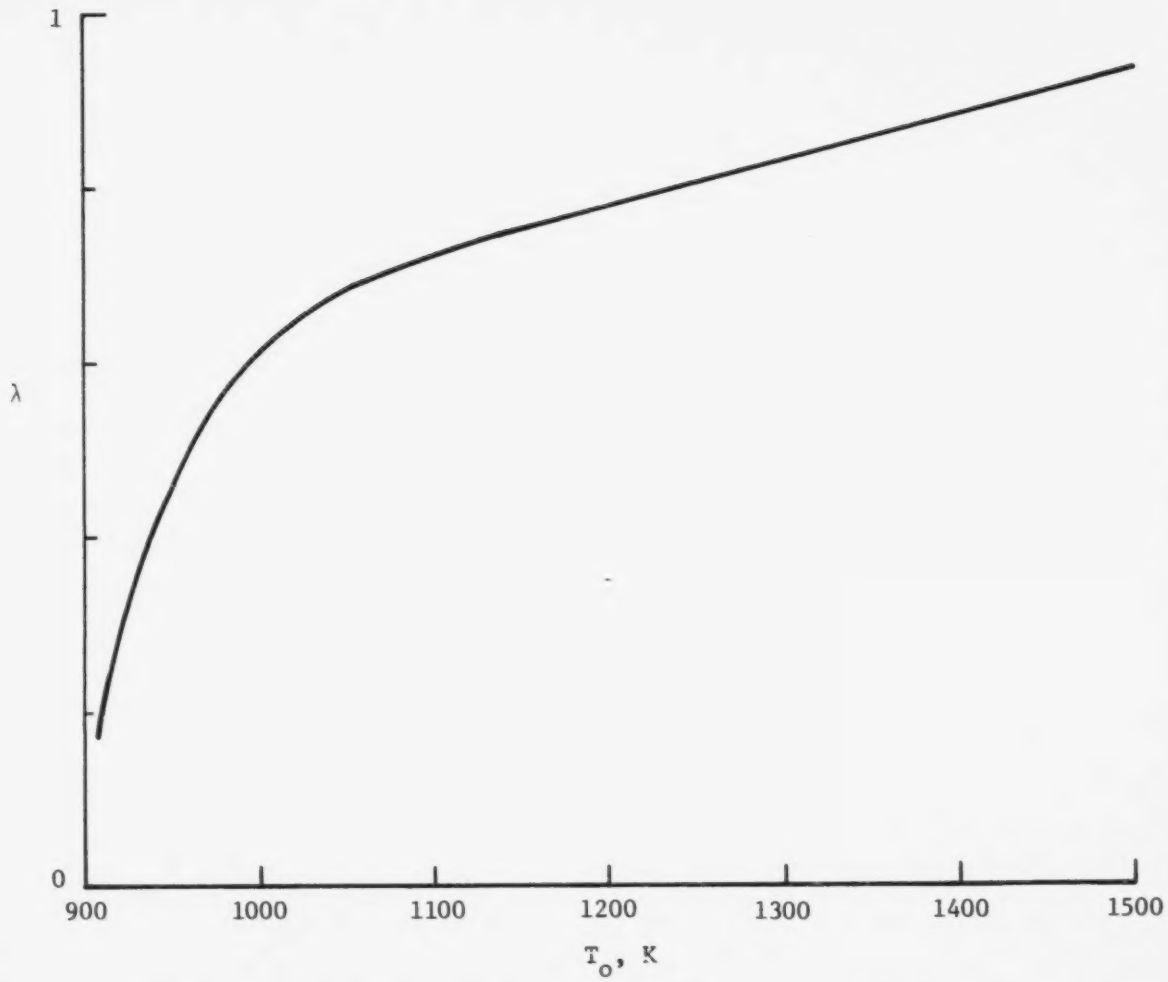


Figure 12.- Reduction of ignition times due to flight contaminant of 10 ppmw O_3. p = 1.0 atm; ϕ = 1.0.

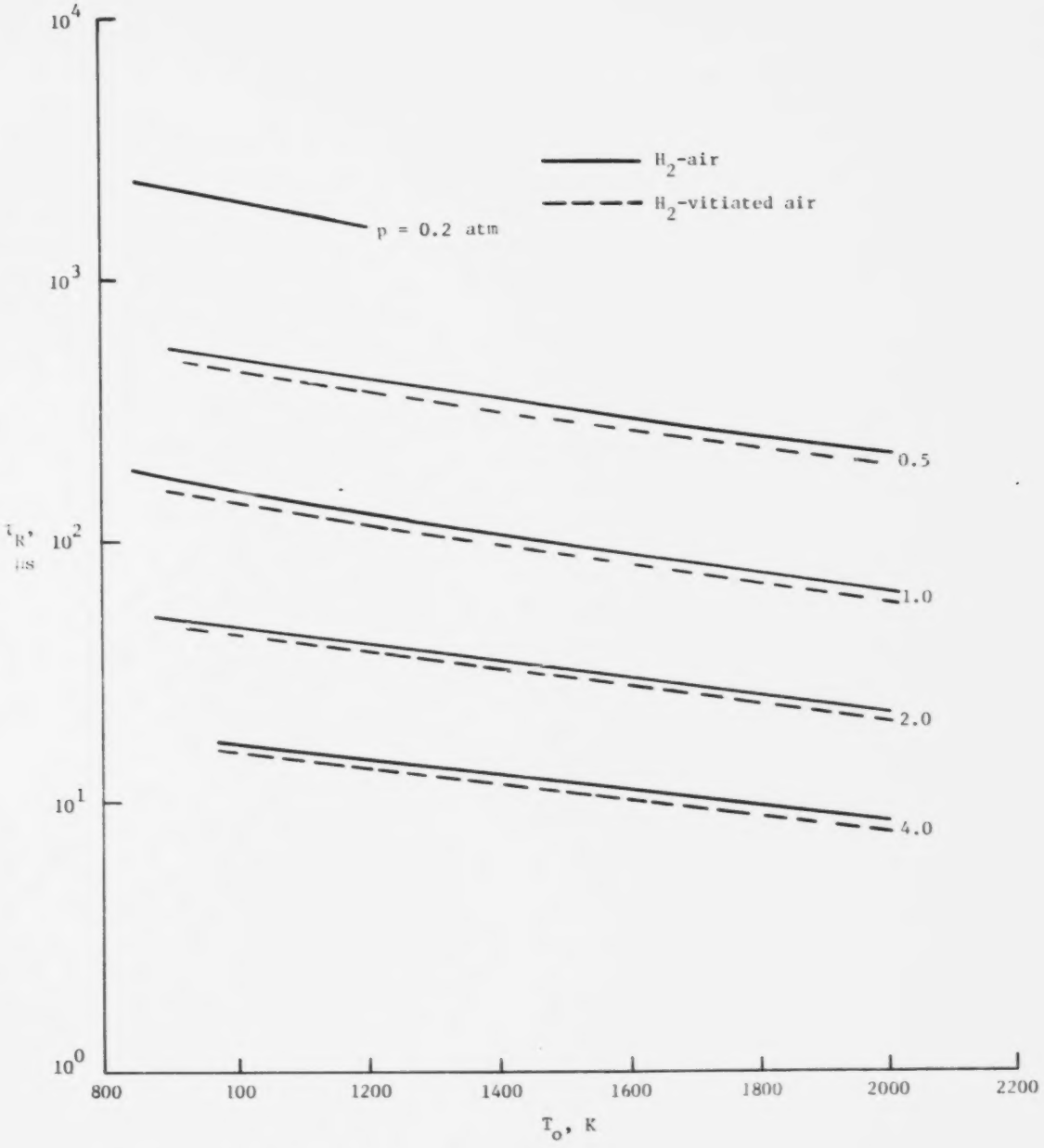


Figure 13.- Reaction times as function of temperature. ϕ = 1.0.

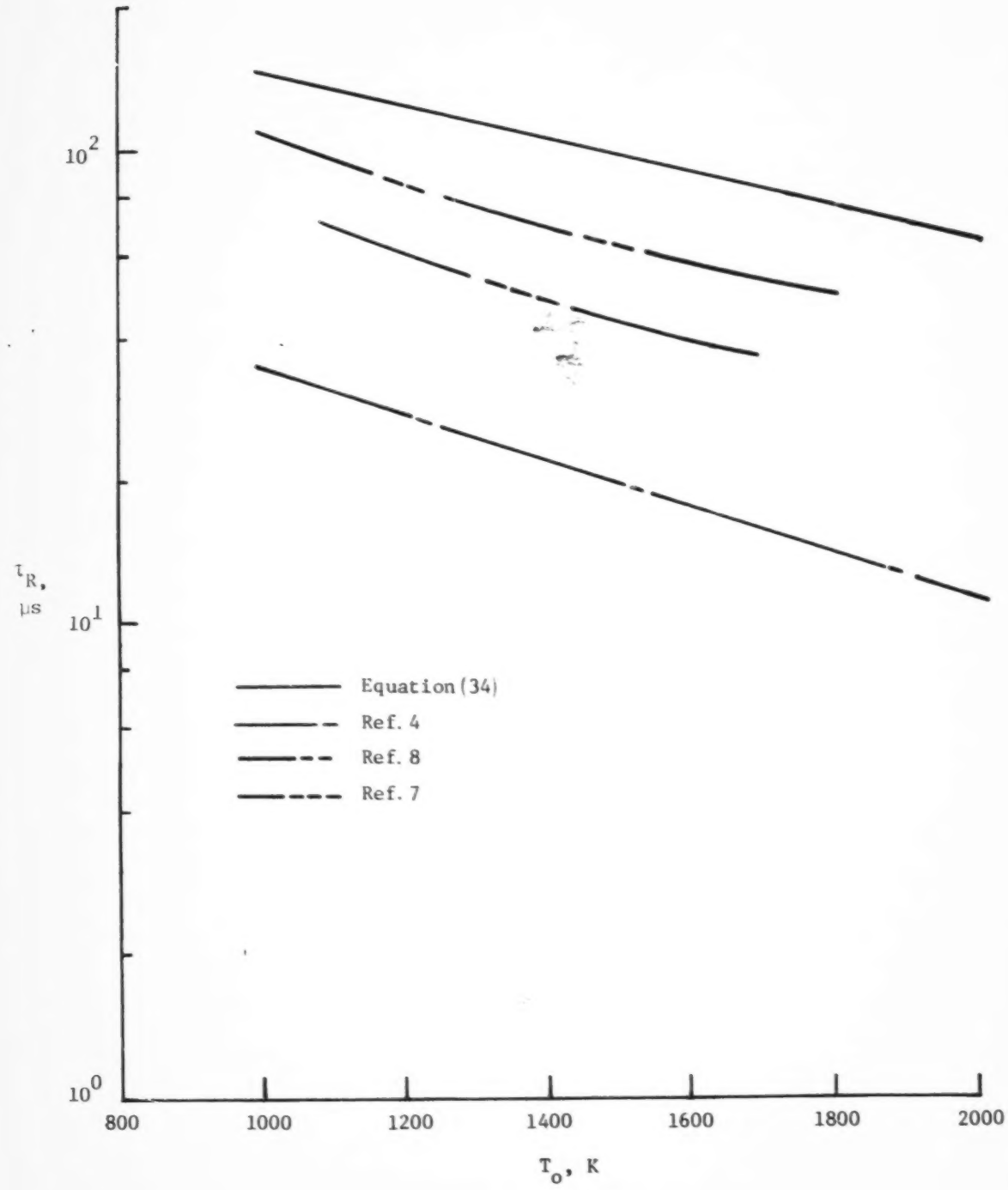
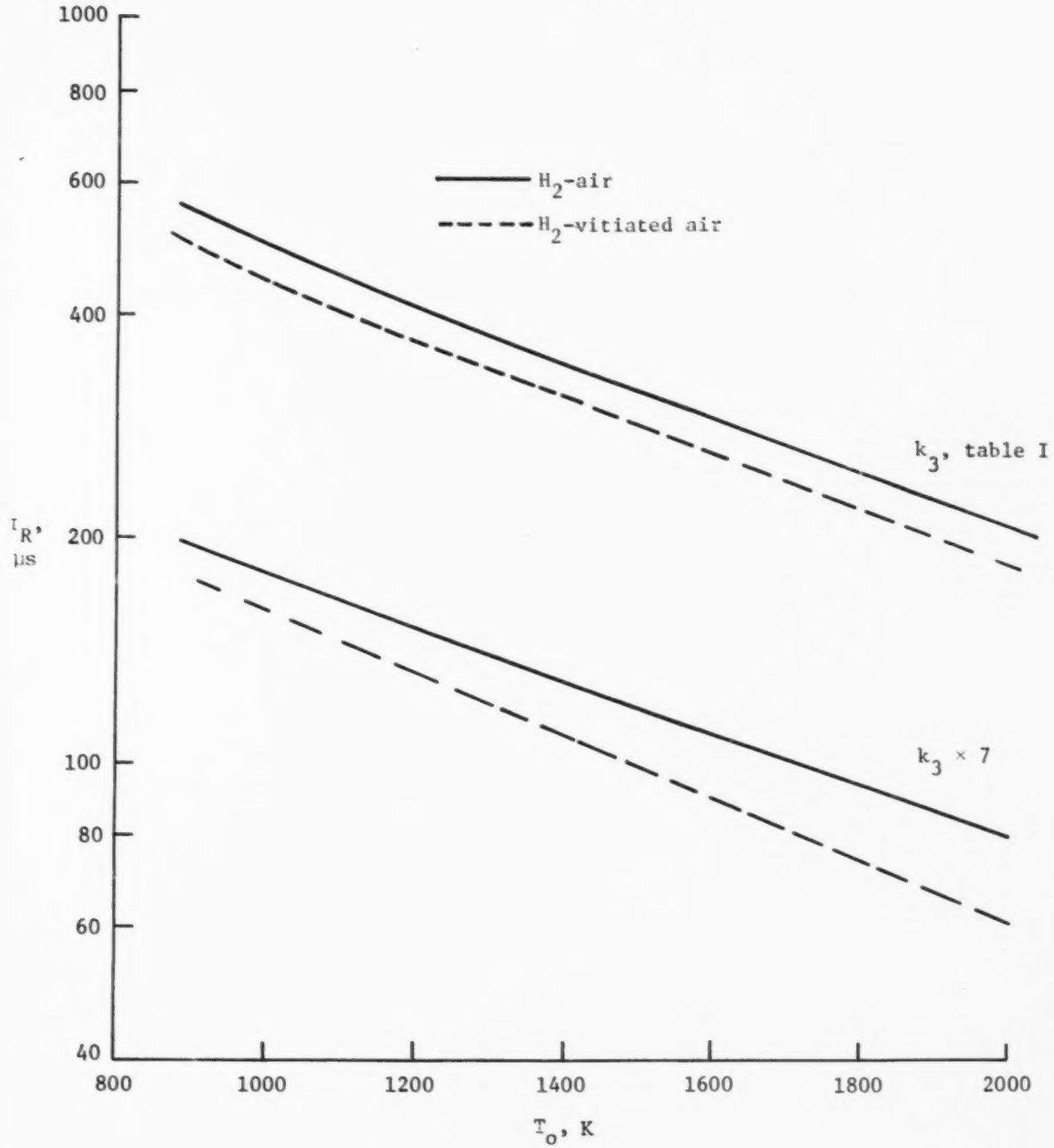
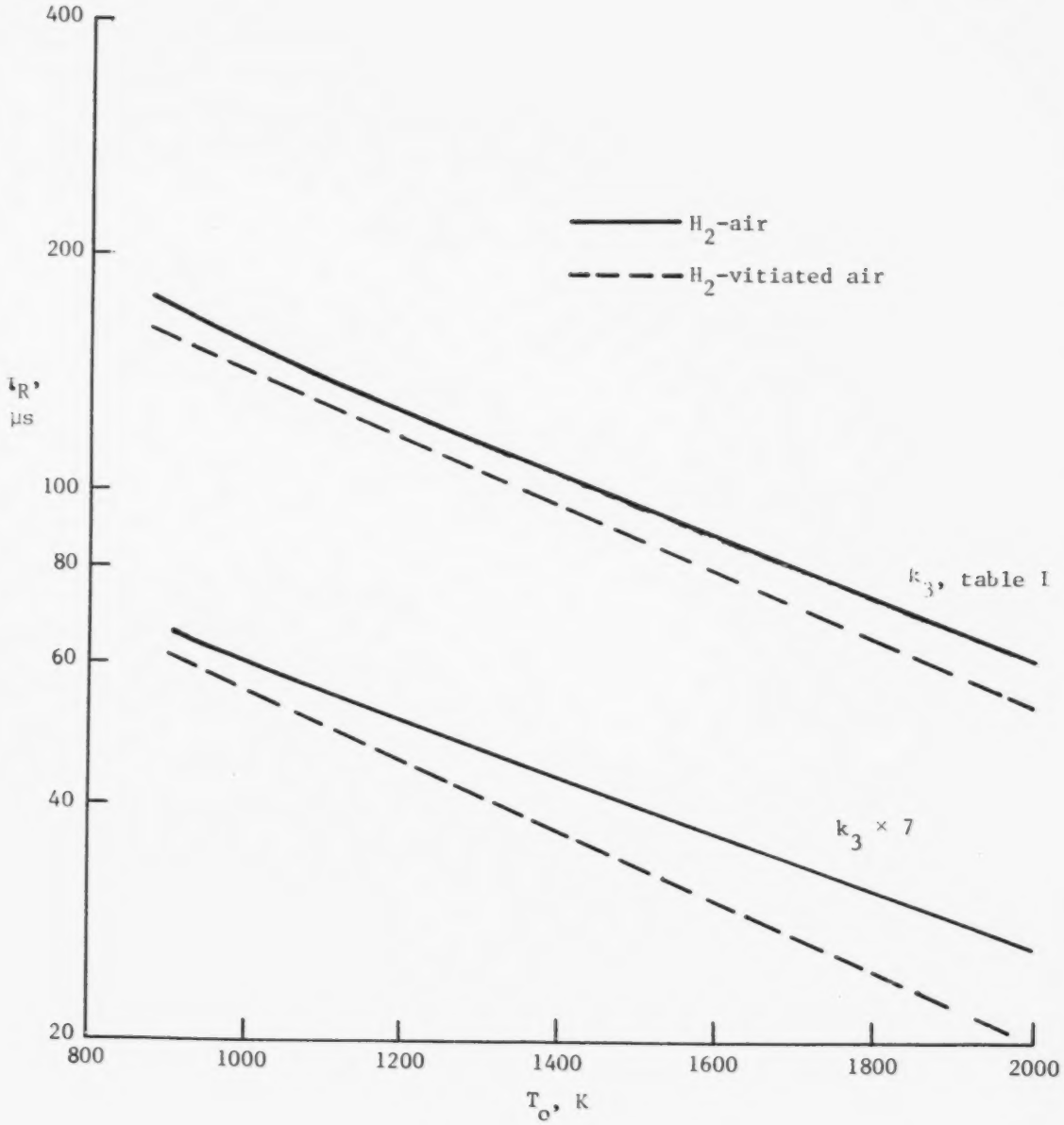


Figure 14.- Comparison of theoretical H_2-air reaction times.
p = 1.0 atm; ϕ = 1.0.



(a) p = 0.5 atm.

Figure 15.- Effect of rate constant of H + OH + M → H_2O + M on reaction times for H_2-air and H_2-vitiated air at ϕ = 1.0.



(b) p = 1.0 atm.

Figure 15.- Concluded.

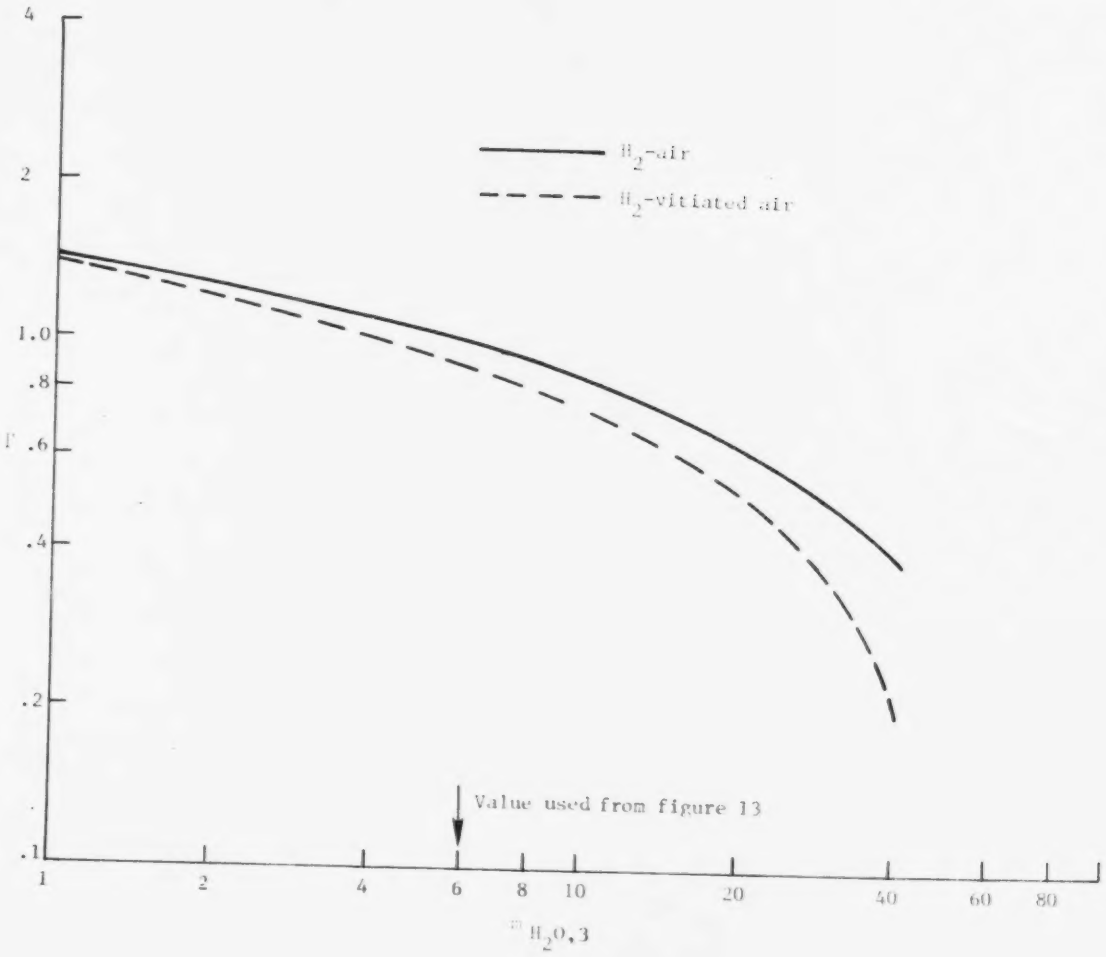


Figure 16.- Effect of third-body efficiency of H_2O in reaction $H + OH + M \rightarrow H_2O + M$ on reaction time. T_o = 1500 K; p = 1 atm; $\phi \cong 1.0$.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TP-1856		

4. Title and Subtitle	5. Report Date
CHEMICAL KINETIC ANALYSIS OF HYDROGEN-AIR IGNITION AND REACTION TIMES	July 1981
	6. Performing Organization Code: 505-32-93-01
7. Author(s): R. Clayton Rogers and Charles J. Schexnayder, Jr.	8. Performing Organization Report No.: L-14379
	10. Work Unit No.
9. Performing Organization Name and Address: NASA Langley Research Center, Hampton, VA 23665	11. Contract or Grant No.
	13. Type of Report and Period Covered: Technical Paper
12. Sponsoring Agency Name and Address: National Aeronautics and Space Administration, Washington, DC 20546	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

An analytical study of hydrogen-air kinetic was performed. Calculations were made over a range of pressure from 0.2 to 4.0 atm, temperatures from 850 to 2000 K, and mixture equivalence ratios from 0.2 to 2.0. The finite-rate chemistry model included 60 reactions in 20 species of the H_2-O_2-N_2 system. The calculations also included an assessment of how small amounts of the chemicals H_2O, NO_x, H_2O_2, and O_3 in the initial mixture affect ignition and reaction times, and how the variation of the third-body efficiency of H_2O relative of N_2 in certain key reactions may affect reaction time. The results indicate that for mixture equivalence ratios between 0.5 and 1.7, ignition times are nearly constant; however, the presence of H_2O and NO can have significant effects on ignition times, depending on the mixture temperature. Reaction time is dominantly influenced by pressure but is nearly independent of initial temperature, equivalence ratio, and the addition of chemicals. Effects of kinetics on reaction at supersonic combustor conditions are discussed, and recommendations for further experimental studies of rate constants for key reactions are included.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Ignition time Reaction time Chemical kinetics Hydrogen reaction	Unclassified - Unlimited Subject Category 25

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	52	A04

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